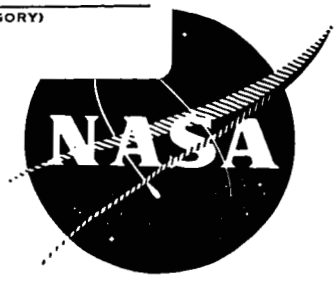
NASA CR 54806



(FINAL REPORT)

DEVELOPMENT OF CADMIUM SULFIDE THIN FILM PHOTOVOLTAIC CELLS

BY

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F. AUGUSTINE, W. K. BOWER

PREPARED FOR

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 3-6461

November 15, 1965

ELECTRONIC RESEARCH DIVISION

CLEVITE CORPORATION

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SUMMARY

The severe curling of the CdS film-plastic substrate combination has been solved by laminating a second plastic layer on the other side of the CdS film. A highly conducting and strongly bonded coating was developed for the plastic substrate. With the Clevite barrier formation process this has resulted in large area frontwall plastic substrate cells with initial conversion efficiencies of 4 to 6% reproducibly.

Coupled with decreases in CdS and plastic layer thicknesses these higher outputs have led to substantial increases in the power to weight ratio of the CdS thin film solar cell. One 50 cm^2 area cell has yielded 106 watts per pound.

The performance and stability now appear to be essentially equivalent for both the metal substrate and plastic substrate constructions of the CdS thin film solar cell. Difficulties in fabrication have led to the postponement of further work on the backwall and backwall-frontwall combination cell constructions.

Extensive studies have led to the conclusion that the major factor in CdS film cell degradation has been the pressure contact of the grid to the cell barrier. A method of attaching the grid with a conductive adhesive has been developed which shows promise of getting around this difficulty, though so far cells with cemented grids have shown an unexpected tendency to degrade in output when exposed to prolonged temperature cycling.

INTRODUCTION

This report summarizes the work performed on Contract NAS 3-6461. This contract provided for the continuation of a program[1] to develop a backwall plastic substrate CdS thin film solar cell. The objective was the development of the plastic substrate cell to obtain conversion efficiencies greater than 4% reproducibly. Soon after the work on this contract started, separate Company funded work to acquire a facility for making frontwall metal substrate CdS solar cells yielded an improved barrier formation process which raised the output of frontwall metal substrate cells to the 4 to 6% range reproducibly.

However, some of these cells were not stable, and some of the design features were not satisfactory for space application. Therefore, additional funding was provided on the plastic substrate cell contract and the statement of work was revised to include work on the stability problems and design features of the frontwall metal substrate cell. Prospects for the frontwall plastic substrate cell became brighter and provisions were made also for work on that construction.

CELL CONSTRUCTION

a. Backwall Glass Substrate Cell

The first successful CdS thin film solar cells[2, 3, 4] were backwall cells formed on glass substrates, one surface of which was made conducting by a pyrolytically deposited SnO_2 coating. The cross section of this type of cell is illustrated in Fig. 1. The glass substrate is about 1/32" thick soft lime or pyrex glass. The barrier layer on the upper surface of the vacuum deposited CdS film is contacted by an air drying conducting silver paint which covers the whole surface.

These cells are thick, heavy and inflexible because thinner glass substrates are not practical. A number of different approaches have been made at several laboratories in an effort to realize flexible light weight thin film solar cells from CdS polycrystalline layers.

b. Backwall Plastic Substrate Cell

Some of the first attempts to achieve a true light weight thin film CdS solar cell were by the use of a plastic substrate.[5, 6] Best results were obtained with a high temperature polyimide plastic.[7] The cell construction is illustrated in Fig. 2. In principle it is similar to the glass substrate cell. It is illuminated through the substrate and CdS layer to the barrier. The response is extrinsic only.

There were practical difficulties with this cell construction during the early trials. There were difficulties with curling and even greater difficulties with high series resistance which limited cell output. This latter difficulty was studied at great length during the preceding contract.[1]

Further attempts were made early in this contract to reduce the series resistance of the n-type CdS layer. One method was through the use of a double layer CdS film -- a low resistivity layer for the bulk of the film topped by a high resistivity layer on which the barrier was formed. In principle this approach should work but in practice it was found that adequate control could not be exercised over the evaporation process. A few good films were obtained and these gave good cells, but they could not be reproduced regularly at the state of the art of evaporation which had then been attained.

Another method tried to reduce series resistance was the use of grids, either above or below the CdS film. Good results were obtained in a few cases with a fine electroformed metal mesh partially embedded in the plastic substrate on which the CdS layer was evaporated. This construction is illustrated in Fig. 3. It was difficult to secure reproducible results from this approach also. The grids frequently separated from the substrate at places and would stick through the CdS film. If the grids were cemented to the substrate with epoxy it was difficult to adequately clean the gridded substrate prior to CdS film deposition and poor CdS film adhesion, or poor film structure would result.

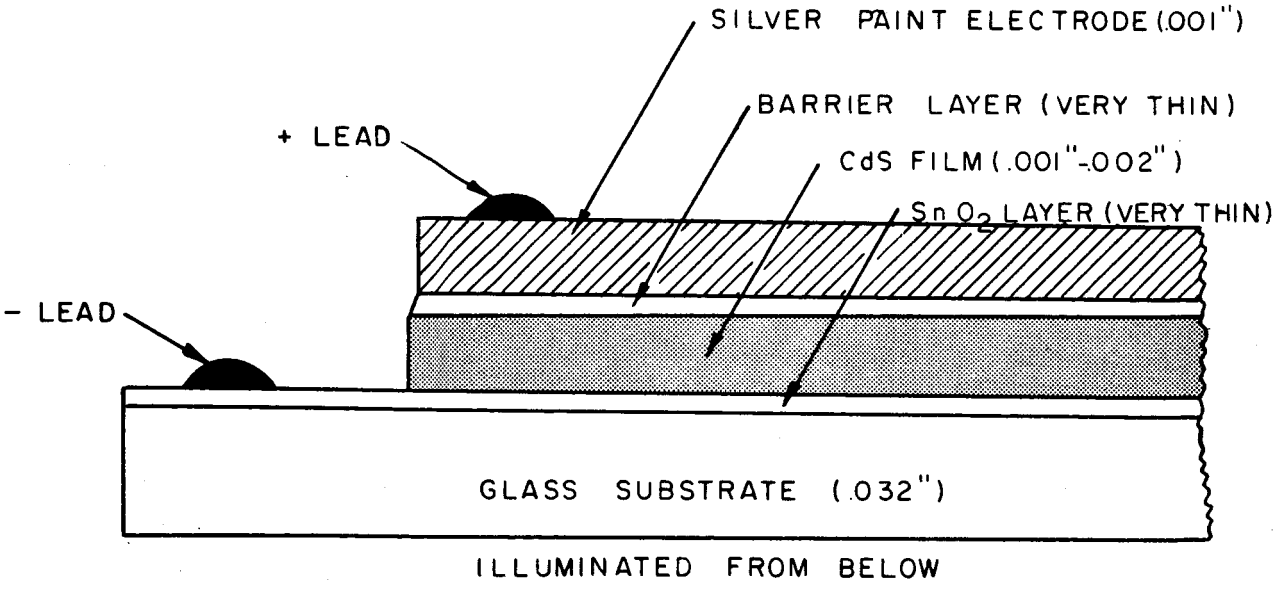


FIG. 1. BACKWALL CdS FILM SOLAR CELL ON GLASS SUBSTRATE.

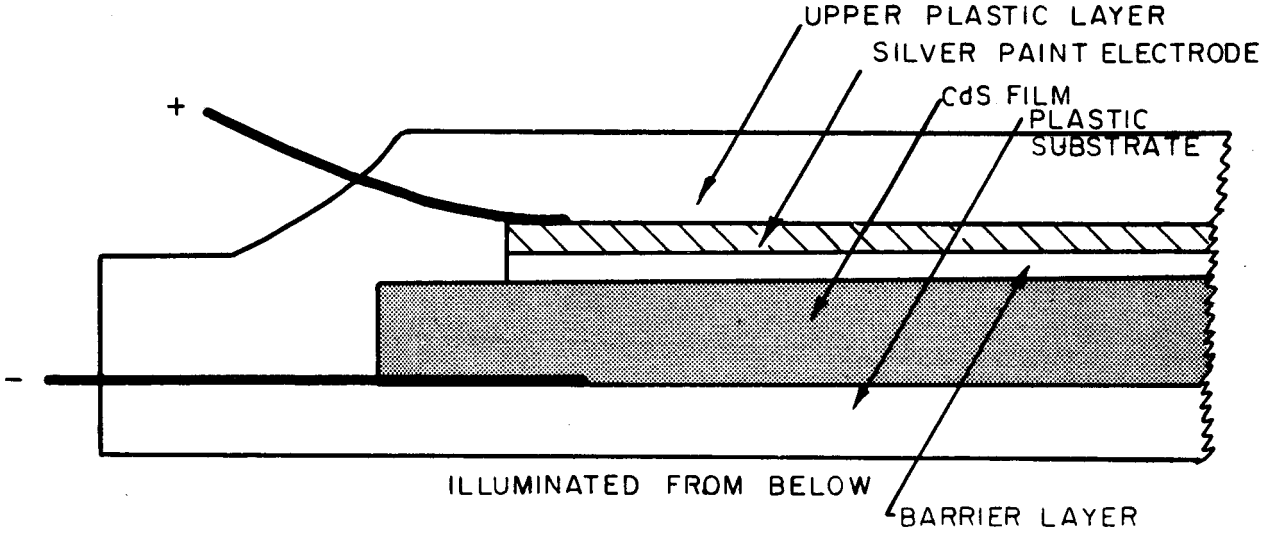


FIG. 2. BACKWALL CdS FILM SOLAR CELL ON PLASTIC SUBSTRATE

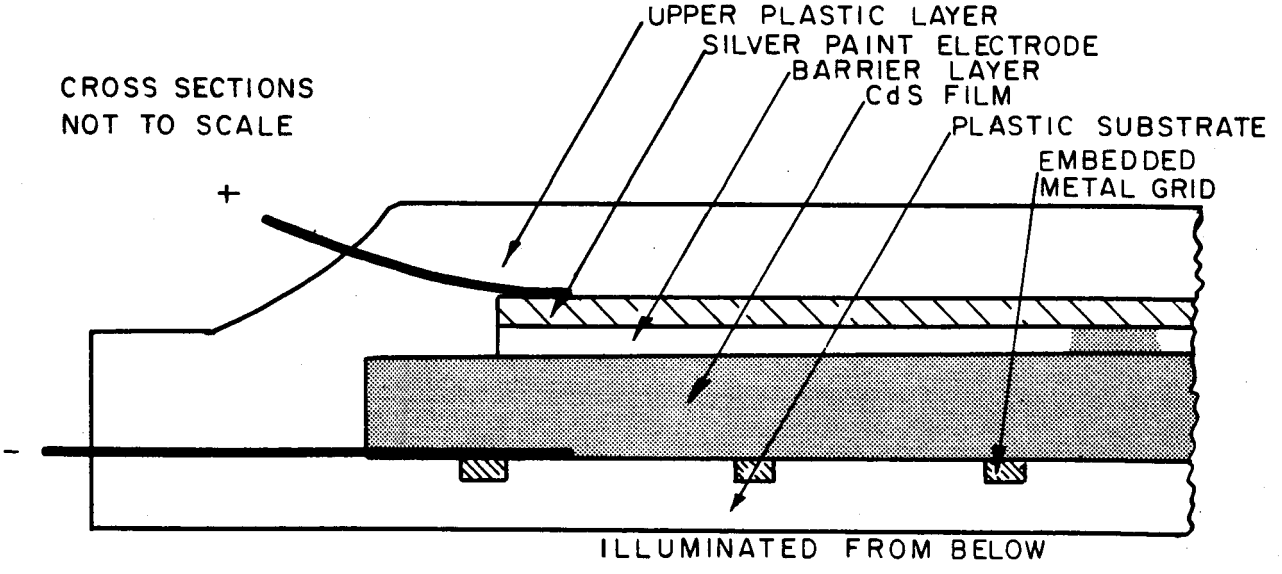


FIG. 3. BACKWALL CdS FILM SOLAR CELL ON PLASTIC SUBSTRATE WITH EMBEDDED GRID

c. Combination Backwall-Frontwall Plastic Substrate Cell

This construction is a modification of the backwall plastic substrate cell, with an embedded grid beneath the CdS film and a second metal mesh grid laminated in contact to the barrier above the CdS film as illustrated in Fig. 4. This cell is operable in either frontwall or backwall modes and could operate in both modes simultaneously. The design might be useful in unoriented arrays of the paddle wheel type since only half as many cells would be needed for any given power rating. They might also be used in stacked or composite cell arrays.

A few cells of this design were fabricated successfully. At best they gave efficiencies in the range of 2.5 to 3.5%, and had about the same output operated as backwall cells with extrinsic response only as they did when operated as frontwall cells with both extrinsic and intrinsic response.

This construction was as difficult to reproduce as the backwall plastic substrate cell discussed above. It seems probable that both of these constructions can be developed further and made reproducibly. However, since better results were obtained with the frontwall cell constructions, efforts on the combination cell and the backwall cell were not pursued further.

d. Frontwall Metal Substrate Cell

This cell was constructed first at another laboratory[8] using molybdenum metal foil as substrate and a coarse grid on the barrier surface. The grid was ruled on with a conductive silver paint. Cell efficiencies were generally less than 1%. The factor limiting output, in the light of subsequent experience, was almost certainly the sheet resistance of the Cu_2S barrier layer. Later, a fine electroformed metal mesh grid was used[9] instead of the coarse ruled-on grid and cell efficiencies climbed to the 2 to 3% range.

The frontwall metal substrate cell construction is shown in Fig. 5. The grid is held in pressure contact to the barrier by the laminated plastic layer. Grids as fine as 60 to 100 lines per inch are available commercially[10] with light transmissions in the range of 80 to 90%. This revised construction at first gave power to weight ratios of about 10 watts per pound, which was subsequently doubled by the use of thinner CdS films and thinner molybdenum substrates.[11]

Later, the same laboratory developed a technique of leaving the backs of the cells open and chemically milling[12] the molybdenum substrate of the finished cell to thicknesses of a few tenths of a mil. Power to weight ratios by this means were further increased to the range of 40 watts per pound.

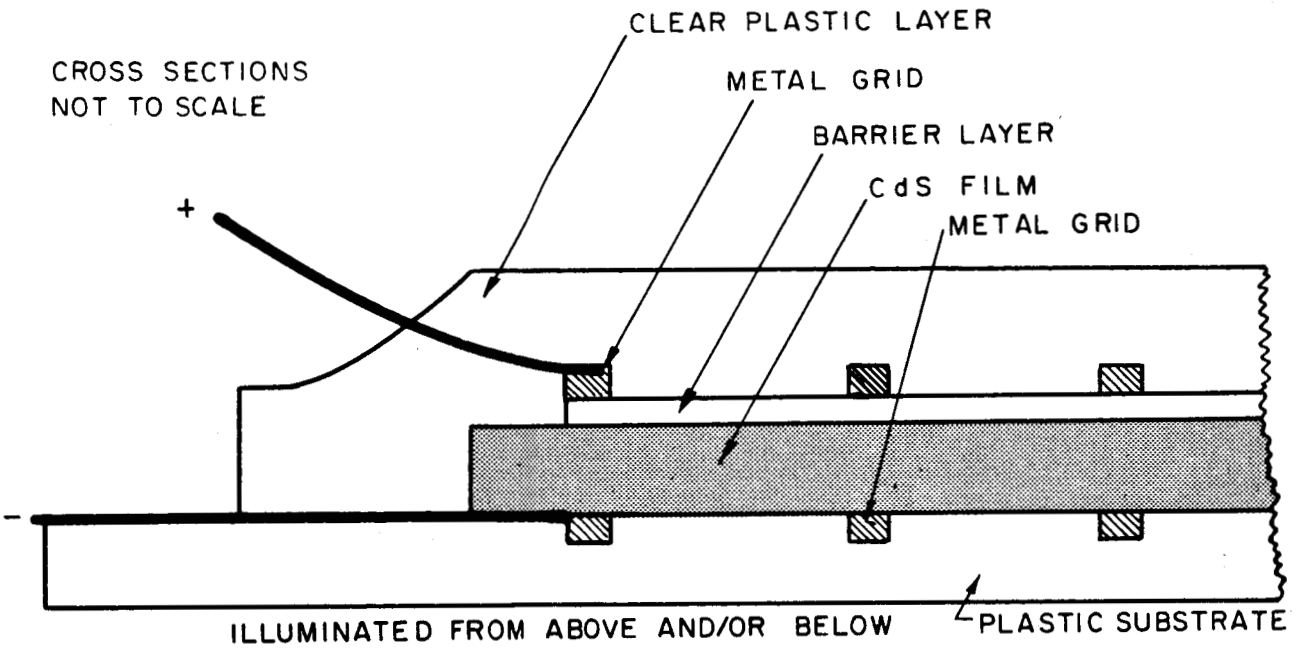


FIG. 4. COMBINATION BACKWALL/FRONTWALL CdS FILM SOLAR CELL ON PLASTIC SUBSTRATE

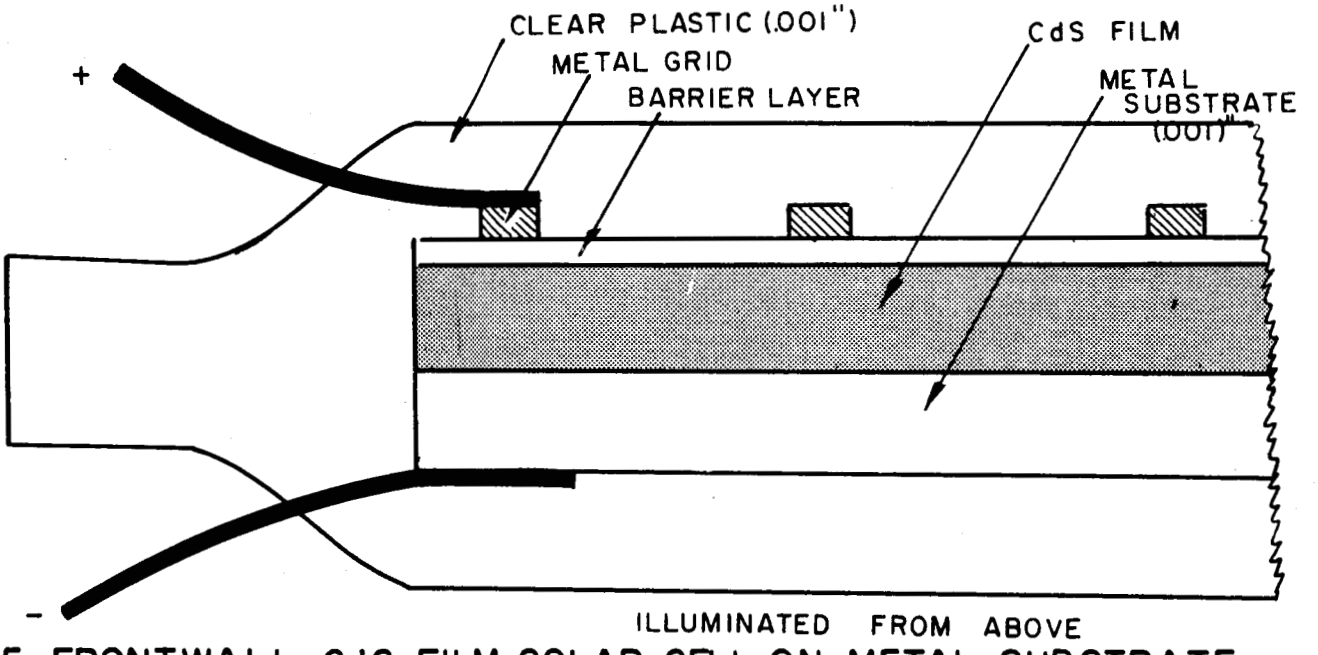


FIG. 5. FRONTWALL CdS FILM SOLAR CELL ON METAL SUBSTRATE

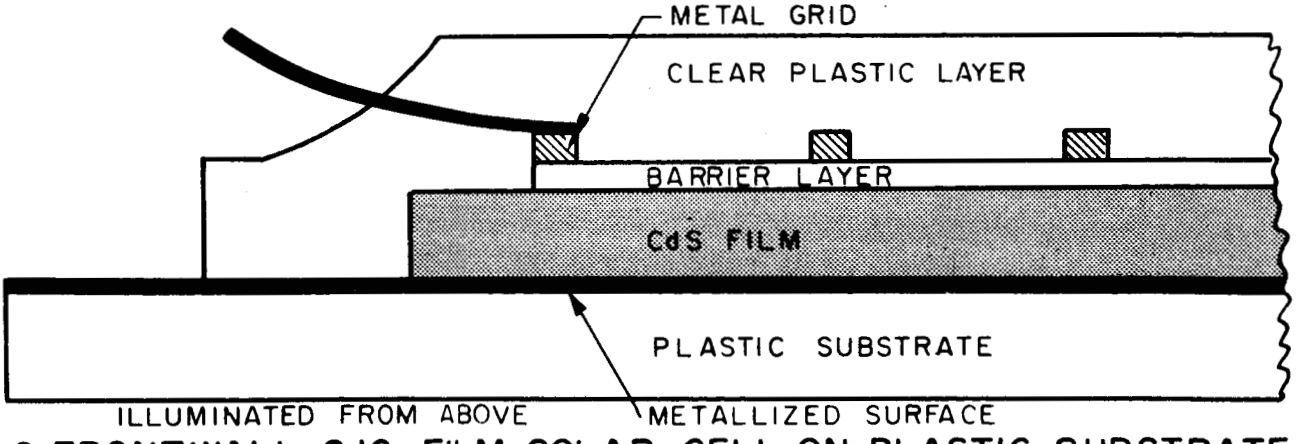


FIG. 6. FRONTWALL CdS FILM SOLAR CELL ON PLASTIC SUBSTRATE

About the time the present contract was beginning, an improved method of barrier formation was developed in this laboratory on an in-house project, which raised the efficiency of the frontwall metal substrate cell[13] to the 4 to 6% range. These cells were of similar construction to the earlier version illustrated in Fig. 5, except that the CdS film was thinner. Encapsulating plastic film thicknesses were also reduced, to as thin as 1 mil. These improvements gave power to weight ratios of 50 watts per pound when chemical milling of the substrate was used.

Work on the frontwall metal substrate cell reported here was performed during the second half of the contract and was concerned with the factors affecting the stability of the cell, and with design variations calculated to yield a thinner lighter weight cell. This work is described more fully in following sections.

e. Frontwall Plastic Substrate Cell

This construction is similar to the frontwall metal substrate cell except that the metal foil substrate is replaced by a metallized plastic film. Metallizing at first was accomplished by the vacuum deposition of gold and similar metal compositions on high temperature polyimide plastic films of about 2 mils thickness. The heaviest metal depositions that could be obtained in this fashion had sheet resistances of 0.3 to 1.0 ohms per square, and consequently the cells were limited in their output due to series resistance on the n-side of the barrier. Large area cells had maximum efficiencies of about 2 to 3%.

A method of securing a very conductive and very adherent layer on the plastic film was developed. This consisted of mixing a silver flake pigment in a polyimide varnish, thinning with a solvent vehicle, spraying onto the polyimide plastic film to a thickness of 0.1 to 0.3 mils, and curing in place. The cured coating was then given a thin zinc plating prior to CdS film deposition to ensure ohmic contact to the CdS. The construction of this plastic substrate cell is shown in Fig. 6.

When the substrates are properly prepared so that a good homogeneous CdS film can be deposited on them, the plastic substrate cells give outputs equal to the metal substrate cells. Special handling of the thin plastic substrates and films is necessary because of their greater flexibility and their greater tendency to curl. In vacuum evaporation, the substrate is clamped in a thin picture-frame type of holder, lightly enough that relative expansion and contraction can take place, but firmly enough to hold the film flat. For barrier formation the films are carefully removed from the frames and allowed to wrap themselves around a glass cylinder for dipping, rinsing, and heat treating.

After barrier formation the cells are contacted with a fine mesh metal grid and laminated with a film of plastic the same thickness as the substrate plastic. With this treatment the cells lie flat and no further special handling is necessary. In production these cells could be processed on a long continuous ribbon held in position for each operation by being stretched between rollers.

SUBSTRATES

a. Molybdenum

The standard metal substrate cells studied on this project were formed on 2 mil thick pure annealed molybdenum foil available commercially from several suppliers. Preparation of the substrate, including cleaning and etching, prior to CdS film evaporation, has been described elsewhere.[14] No particular changes in this process were necessary.

b. Alternate Metal Substrates

A number of different metals have been tried in place of molybdenum as the substrate for frontwall cells. Most attempts have been with the other refractory metals such as tantalum, tungsten, and niobium, since these have thermal expansion coefficients not too far different from CdS. However, these metals all suffer from the same disadvantages as molybdenum, though to varying degrees.

Earlier, some experiments were run with soft ductile metals as CdS cell substrates,[15, 16] including silver and zinc, and some encouraging results were obtained. However, these were not followed up at the time.

On this project silver, copper, and aluminum foils were re-evaluated as substrates for CdS cells. Very poor results were obtained with aluminum and this was not tried further. However, excellent results were obtained with both silver and copper. In both cases a zinc plating was applied to the metal prior to CdS film evaporation to ensure ohmic low resistance contact between CdS and substrate. The metal foils in both cases were nominally 1 mil in thickness and were cleaned and acid etched prior to zinc plating. In view of the lower cost of copper and its greater availability, efforts were concentrated on this material in the last few months of the contract.

Several different hardnesses of copper foil are available as well as various alloys of copper. It was found that better results were obtained with a harder grade of copper than with a very soft grade. An electrolytic copper foil having a Knoop hardness of about 70 to 80 has given good results and has been used for most of the copper substrate cells. Very soft copper presents a handling problem due to its extreme tendency to kink or wrinkle with minor distortion forces. Such kinks and wrinkles are localized regions of very sharp radius of curvature and cause trouble with the CdS film adhesion.

Table I summarizes the initial (highest) output obtained from 18 large area copper substrate frontwall CdS film cells fabricated in the last month of the contract using the best processing techniques and cell design features that had been developed. These were 3" x 3" cells, having an integral extension of the 1 mil copper substrate acting as the negative lead.

TABLE I

LARGE AREA COPPER SUBSTRATE CELL PERFORMANCE

Cell No.	OCV	SCC	J	Eff.	Construction	Wt	Watts/lb
	Volts	Amps	mA/cm	%	(see below)	gms	
A684	.490	.880	17.6	4.9	A	4.16	32
A687	.480	1.120	22.4	6.2	A	4.10	41
A688	.510	.950	19.0	5.4	A	4.00	37
A691	.490	1.160	23.2	6.2	A	3.49	48
A692	.505	.880	17.6	5.6	A	4.28	36
A696	.510	.910	18.2	5.6	A	3.95	37
A699	.490	.965	19.3	5.9	A	4.19	38
A700	.515	.900	18.0	5.7	A	4.29	37
A703	.510	1.080	21.6	6.2	C	2.80	60
A704	.505	1.030	20.6	5.4	C	2.44	52
A706	.515	.955	19.1	6.3	C, D	3.18	54
A707	.525	1.015	20.2	6.4	B, D	3.37	52
D114C	.475	.970	19.4	4.9	C	3.28	41
D114G	.475	1.090	21.8	5.9	C	3.41	46
D114I	.475	.990	19.7	6.0	C	3.48	48
D117A	.510	.990	19.7	5.7	B, D	3.33	47
D117C	.495	1.190	23.8	7.1	B	3.38	57
D117G	.510	1.070	21.4	6.4	B	3.74	47
Avg.	.499	1.008	20.1	5.9		3.60	45

Construction:

A. Laminated with 2 mil Mylar both sides.
B. Laminated with 2 mil Mylar top side only.
C. Laminated with 1 mil Mylar top side only.
D. Etched copper grid.

Tested at 25°C in tungsten light equivalent to air mass 1 sunlight.

Watts per pound calculated for air mass 0 sunlight on basis of 1.20 times the air mass 1 power output.

Most of these cells were laminated with a single 2 mil thick layer of Mylar plastic over the barrier and no plastic beneath. This arrangement gives minimum difficulty with curling.

The lamination conditions were the same as used for the regular molybdenum substrate cells fabricated in the same period. A total of 7 such standard molybdenum cells were made in the same period and gave an average OCV of 0.466 volts, SCC of 0.975 amperes (or 19.5 mA/cm^2), and initial efficiency of 5.5%. The copper substrate cells do appear to give slightly higher outputs than the molybdenum substrate cells, with the most marked difference being the higher voltage.

There has not been time for characterization of the copper substrate cells for stability or for resistance to thermal shock and thermal cycling. A few cells have been on dry shelf storage for periods up to 3 months and appear to be at least as stable as the molybdenum substrate cells.

c. Plastic

As discussed in the section on the frontwall plastic substrate cell construction above, good results were obtained from this cell construction only after the development of a very conductive and adherent coating for the plastic substrate. This coating is made by dispersing silver particles in a polyimide varnish, applying to the cleaned surface of the polyimide plastic film, and curing in place.

The silver pigment[17] used is in flake form and is mixed in equal proportion by weight with the polyimide varnish.[18] This is thinned in a vehicle consisting of equal parts by volume of toluene and dimethylformamide to spray consistency and applied to the cleaned plastic substrate in several thin layers until a total thickness of 0.1 to 0.3 mils has been built up. After drying, to remove the solvent, this layer is cured by heating at 250°C for approximately 30 minutes.

The bond of this coating is extremely tenacious. The sheet resistance is below 0.01 ohms per square, though it may be necessary to burnish the surface of the film to make the measurement. In practice, a light burnishing is given to the coated film with a fine emery paper and then it is given a light zinc coating by electroplating in a zinc fluoborate bath (though equally good results have been obtained by vacuum depositing about 600 A of zinc). The purpose of the zinc plating is to ensure a good low resistance contact for the CdS film.

During the last six months of the contract when the essential features of this process had been worked out, more than a hundred of these large area (3" x 3") plastic substrate cells have been fabricated. They have averaged well over 5% in their initial conversion efficiency.

Most of these have had 2 mil thick substrates. During the last month, 10 of the large area plastic substrate cells had 1 mil thick plastic substrates, while 17 had 2 mil thick substrates. There is no particular difficulty in processing the thinner substrates. Performance of the 2 mil substrate cells is summarized in Table II while that of the 1 mil cells is in Table III. The differences in output between the 1 and 2 mil substrate cells are not believed significant, but the difference in the average power to weight ratio is.

CdS EVAPORATED FILMS

a. Process

The process for CdS film evaporation is the same for the molybdenum, copper, and plastic foil substrates. A commercial luminescent grade of CdS powder is presintered in vacuum to 850°C and in argon to 1200°C in order to densify it and drive off high vapor pressure impurities. It is then ground to pass about a 42 mesh screen. No doping has been used for most of the films evaporated on this project.

The CdS material is then charged into cylindrical tantalum evaporation sources which are heated to about 1050° to 1100°C by passing an electric current through them. Vacua on the order of 10^{-5} to 10^{-6} Torr are used, and the substrates are preheated by radiation to 220°C. The open end of each evaporation source is closed with a finely perforated screen which prevents spattering of the substrate with ejected CdS particles. Deposition rates of 200 to 300 A per second are normally employed and a total film thickness of 15 to 20 microns has generally given best results. Total evaporation time is about 10 to 15 minutes. Approximately 10 minutes is usually taken to reach full evaporation rate, and the system is generally held at full temperature for about 10 minutes after the evaporation is complete to be sure that the sources are empty.

The resultant films should have a glossy reddish color and be sufficiently clear optically to see through them to the underlying substrate. Good films show a high degree of orientation with the c-axes of the crystallites generally perpendicular to the substrate. Accurate determinations of crystallite size of these films have not been made.

There do appear to be differences in the films which are deposited on molybdenum substrates and those deposited on plastic substrates. The films on plastic substrates appear to be more highly stressed and to have a higher dislocation density, though only preliminary qualitative studies have been made of these factors.

b. Double Layer Films

The double layer CdS film was investigated as a possible means of securing very low resistance CdS films without adversely affecting the quality of the junction. This approach was believed essential to the success of the backwall plastic substrate cell where the substrate was nonconducting.

TABLE II
PERFORMANCE OF LARGE AREA PLASTIC SUBSTRATE FRONTWALL CELLS ON 2 MIL SUBSTRATES
(Fabricated in Last Month of Contract by Standardized Process)

Cell No.	OCV	SCC	J	Max. Power	Eff.	Weight	Watts/lb
	Volts	Amps	mA/cm^2	Watts	%	gms	
D99A	.440	0.830	16.6	.200	4.0	2.99	36
D100A	.470	1.060	21.2	.295	5.9	2.50	65
D100C	.465	1.060	21.2	.287	5.8	2.45	64
D100G	.480	0.925	18.5	.305	6.1	2.72	61
D100I	.470	1.110	22.1	.335	6.7	2.49	73
D102A	.470	1.040	20.8	.325	6.5	2.37	75
D102C	.463	0.780	15.6	.225	5.0	2.35	52
D102G	.462	1.030	20.6	.345	6.9	2.33	81
D102I	.450	1.100	22.0	.255	5.6	2.31	60
D107A	.475	0.990	19.8	.315	6.2	2.48	69
D107C	.475	0.980	19.6	.290	5.8	2.61	60
D107G	.480	0.995	19.9	.295	5.9	2.46	65
D107I	.470	0.960	19.2	.280	5.6	2.55	60
D113A	.472	0.890	17.8	.260	5.1	2.43	58
D113C	.478	0.890	17.8	.280	5.6	2.42	63
D113G	.480	1.015	20.3	.310	6.2	2.43	69
D113I	.465	0.930	18.6	.250	5.0	2.37	57
Avg.	.469	0.976	19.5	.285	5.75	2.49	63

3 Cells scrapped.

TABLE III
PERFORMANCE OF LARGE AREA PLASTIC SUBSTRATE FRONTWALL CELLS - 1 Mil SUBSTRATES
(Fabricated in Last Month of Contract by Standardized Process)

Cell No.	OCV	SCC	J	Max. Power	Eff.	Weight	Watts/lb
	Volts	Amps	mA/cm^2	Watts	%	gms	
D104A	.470	0.980	19.6	.290	5.8	2.00	79
D104C	.475	0.935	18.7	.270	5.4	2.08	71
D104G	.465	1.055	21.1	.320	7.1	1.94	89
D104I	.482	1.065	21.3	.350	7.0	2.12	89
D109A	.480	0.930	18.6	.245	4.9	1.92	70
D109C	.480	0.885	17.7	.230	4.6	1.96	64
D109G	.480	0.930	18.6	.270	5.4	2.12	69
D109I	.475	0.940	18.8	.280	5.6	2.08	73
D115A	.470	0.870	17.4	.190	3.8	1.67	62
D115C	.470	1.015	20.3	.287	5.7	1.88	83
Avg.	.475	0.961	19.2	2.73	5.53	1.98	75

2 Cells scrapped.

The idea was to use a highly doped CdS layer next to the substrate that would carry the bulk of the current laterally along the film to the negative lead with minimum voltage drop, and to top this with a very thin high resistance CdS layer on which the barrier would be formed. The high resistance upper layer would yield a high open circuit voltage cell and could presumably be kept thin enough so that the voltage drop through the film to the low resistivity layer beneath would be negligible.

The highly conducting CdS film was secured by doping the CdS starting material with indium. Various amounts of doping were tried and it was found that with . 067 mol percent of indium in the charge, the bulk resistivity of the evaporated CdS film was in the range of 0. 01 ohm-cm, and the optical transmission was reduced by less than 10%.

The high resistivity layer was obtained by using undoped CdS and by adding small amounts of copper counterdoping to the starting CdS charge material. Resistivities of about 100 ohm-cm were the goal, but were difficult to obtain reproducibly. It was relatively easy to reproduce the lower resistivity level films.

A number of double layer films were processed on molybdenum foil substrates to test the validity of the approach and to work out the process. A total CdS film thickness of 1 mil was chosen with each layer representing about half of the total. The cells fabricated from these films gave slightly lower outputs than the regular single layer films processed at the same time. The voltage was about the same but the currents were less and there was higher series resistance for the double layer films.

When it was attempted to deposit the double layer films on insulating plastic substrates, relatively poor cells were obtained. It appeared that the films were of generally poorer structure. It was not clear whether this was because of the different properties of the plastic surface on which the CdS films were deposited or to the different evaporation rates used for the double layer films.

At about this time much better results were being obtained with the frontwall plastic substrate cell construction. Hence, the work on the double layer films was curtailed and the extra effort applied to the conducting plastic substrate films.

c. Thinner Films

Better structured films are generally obtained from the use of high substrate temperatures. This yields very adherent films, but low deposition rates result. The yield of CdS material deposited is low. On the other hand it is probable that the characteristics of the devices fabricated from such better structured films would be improved and that much thinner films would be practical. There have been indications that good semiconductive devices can be made from well structured CdS films as thin as 1 micron.[19, 20, 21] In this program two approaches were tried to secure and use thinner CdS films for large area solar cells.

1. Very Thin Films (1 to 5 microns)

This approach consisted of depositing the CdS film at a substrate temperature of 600°C. At this temperature it was found necessary to dope the films and to use the hot wall closed chamber evaporation technique. It was found that the cleanliness of the substrate was more critical when evaporating at high substrate temperatures.

The doping was with indium added to the charge (as In_2S_3) at about 0.05 to 0.07 mol%. The films had resistivities between 10 and 100 ohm-cm. The hot wall closed chamber method is evaporation in a small inner semiclosed chamber, the walls of which are heated to reduce deposition on the walls, and in which a partial pressure of the evaporating constituents builds up. These conditions favor deposition on the substrate. The arrangement is illustrated in Fig. 7.

With the substrate at 600°C and the wall at 550°C, uniform films about 5 microns thick were obtained readily on 2 mil molybdenum foil substrates. These were free from pinholes, spatter or other flaws. The adhesion was excellent and there was no tendency to curl. Figure 8 shows the structure of one such film as disclosed by the electron microscope. The grains are smooth surfaced, well delineated, and up to 5 to 10 microns across. Similar film structures have been observed by other workers.(22)

A number of such very thin films have been deposited on molybdenum foil substrates and processed into small area (1 x 2 cm) solar cells. All films thinner than about 4.5 microns shorted when barriers were processed on them even though the dip time was reduced to 1 second and no pre-etch was employed. Films of 4.5 to 6.5 microns thickness gave cells with efficiencies up to 3.3%. These had good open circuit voltages and good fill factors. The currents were low probably because of incomplete activation with the very short dip times that were employed.

The 5 micron thick films can probably be developed to yield high cell efficiencies over large areas. More effort is required however to work out the detailed technology that will make this practical. This effort is believed well worthwhile since films of this thickness could probably be formed on substrates of comparable thickness and thus yield a really thin very flexible light weight solar cell.

2. Moderately Thin Films (5 to 10 microns)

This approach consisted of depositing the CdS film on a substrate held at 350°C. Again, it was desirable to dope the CdS with indium, though a much lighter doping was used, and in a few cases fair results were obtained without any deliberate doping. The hot wall closed chamber technique was not used for this approach. The tooling was the same as normally employed for 220°C substrate temperature depositions.

A few films of about 11 microns thickness were obtained which gave 1 x 2 cm cells with efficiencies of 4.5, 5.0, and 5.3% using barrier dip times comparable to normal practice (5 seconds). These cells

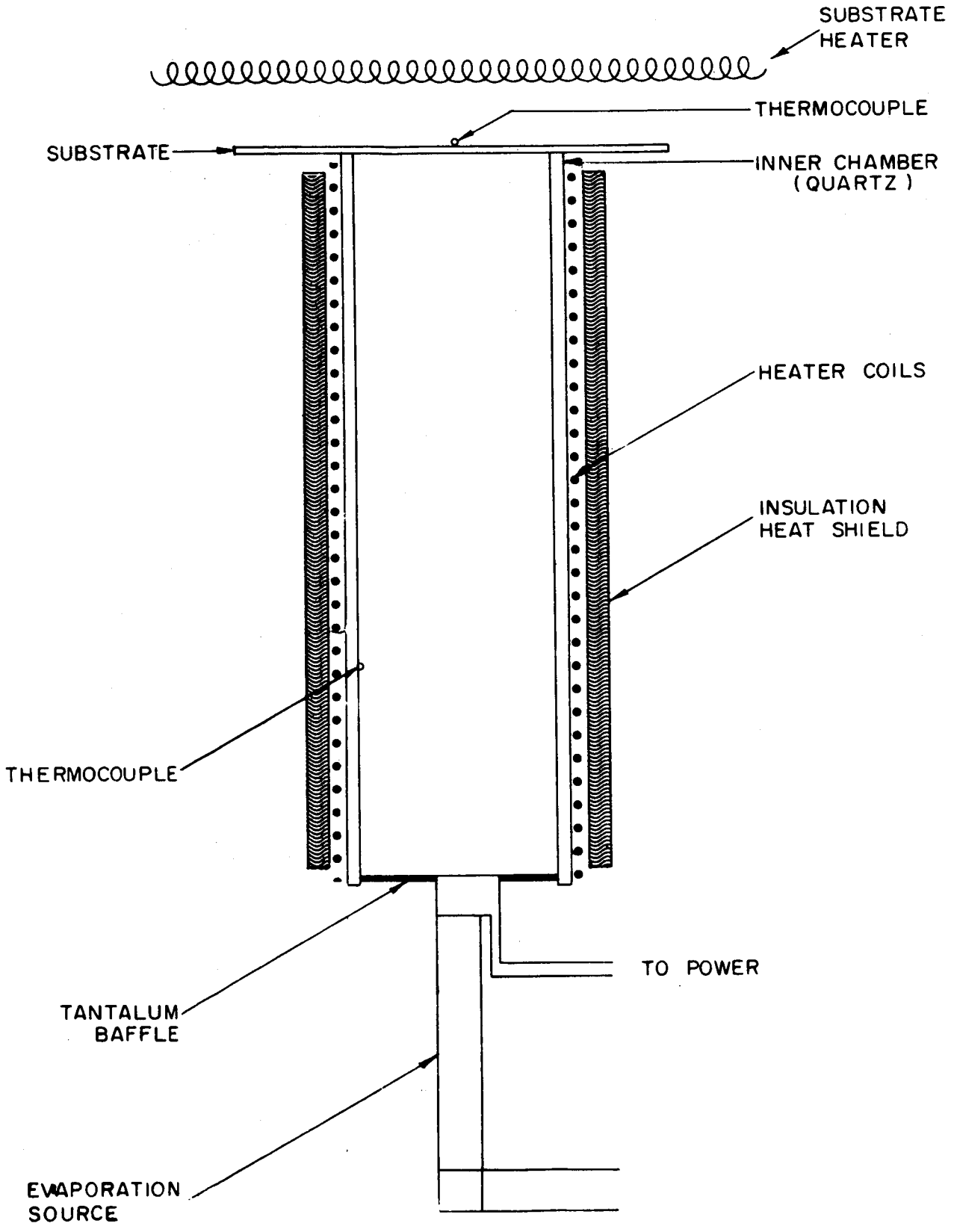
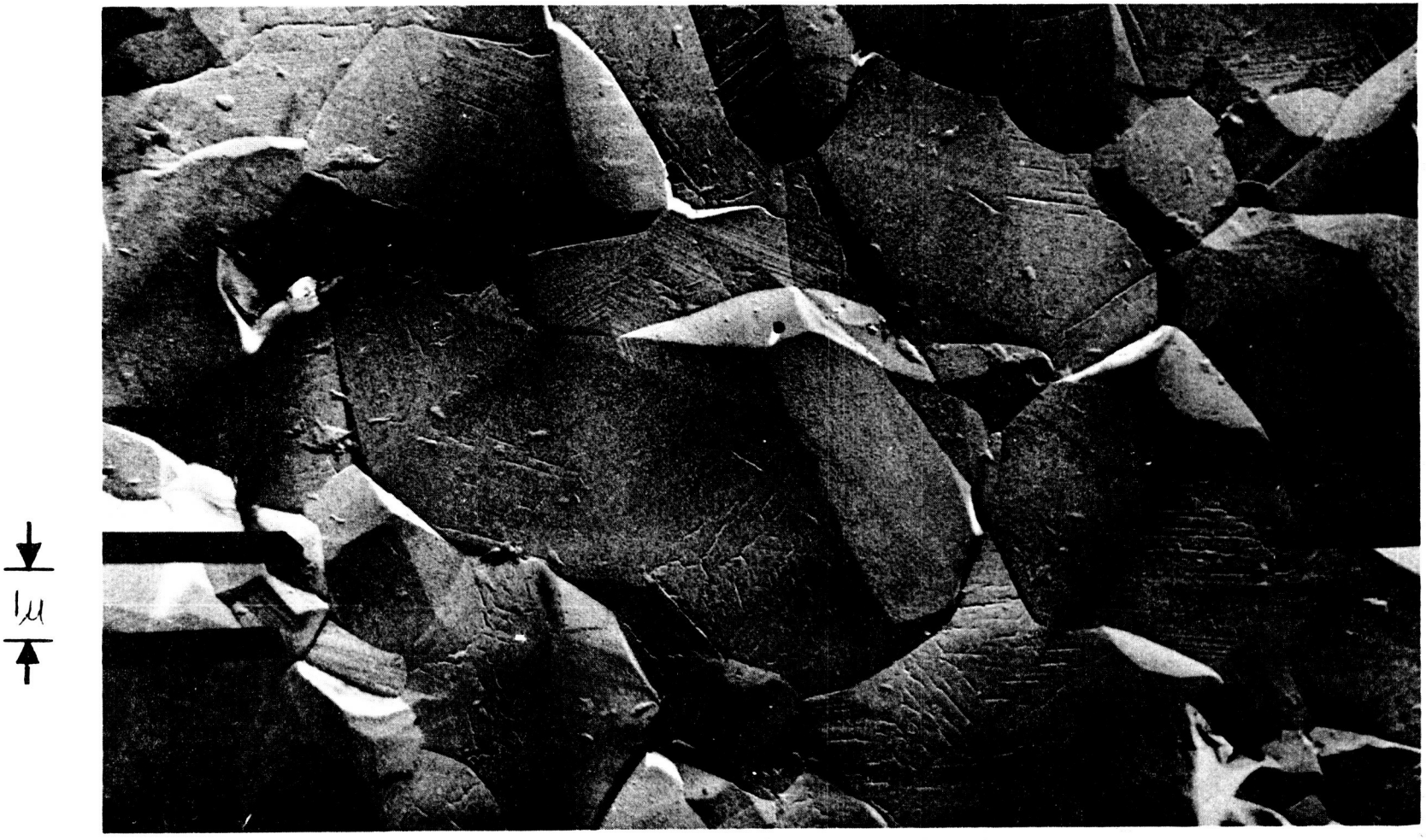


FIG. 7. TOOLING FOR EVAPORATION OF CdS FILMS AT HIGH SUBSTRATE TEMPERATURES.



9800X

FIGURE 8: STRUCTURE OF CdS FILM EVAPORATED AT 600° C SUBSTRATE TEMPERATURE

Film C-74 Etched 8 sec. in 1:3 HCl Solution - Palladium Shadowed Carbon Replica

had good voltages and good fill factors, and short circuit current densities of 16.5 to 17.5 mA/cm^2.

These results also are very encouraging and it is believed these should be developed further.

BARRIER FORMATION

a. Slurry vs. Chemi-Plated Barrier Process

Various methods of forming barriers on CdS crystals and CdS polycrystalline films have been developed. The original method discovered by Reynolds[23, 24] consisted of electroplating copper from a Cu_2SO_4 bath, oxidizing in place and heat treating. This method was subsequently modified[25, 26] for larger area cells and more reproducible results. Other methods of forming barriers on CdS included vacuum evaporating copper[27, 28] and oxidizing in place, the deposition of Cu_2O or Cu_2S from slurries[29] followed by heating, the chemical spray deposition of Cu_2S,[30,31] and the chemi-plating of Cu_2S by means of ion transfer.[32, 33]

The slurry deposition of Cu_2O and Cu_2S was further developed by Augustine[34] to the point where it produced cell efficiencies equivalent to those obtained from the electroplating method. Later, Hietanen[35] developed the chemi-plating process to the point where it produced higher output CdS cells than had been obtained previously.

During this contract a comparison was made between the Cu_2O slurry deposited process and the Cu_2S chemi-plating process on both back-wall and frontwall cells. Nearly identical results were obtained for the two methods of barrier formation. It now appears probable that the slurry process is in reality a chemi-plating process -- the difference in the two methods being the source of the cuprous ions.

What is believed to occur is that cuprous ions displace cadmium at the CdS surface resulting in a semicontinuous layer of Cu_2S in intimate contact with the CdS. The Cu_2S is evidently copper deficient and strongly p-type semiconducting. It is suspected that some copper diffuses a very short distance into the CdS lattice, probably in close association with chloride ions, to form photon absorbing-electron trapping centers, but this has not been proved.

Whatever this structure really is, it appears to be achievable by a number of different techniques though some are a lot more effective than others. The conditions of barrier formation can be relatively critical for maximum results, yet the barriers once formed seem to be amazingly sturdy.

The process developed for chemi-plating the CdS solar cell barrier has proven to be the most convenient and reproducible method for obtaining high efficiency cells and was therefore adopted for all cells processed after the first few months of this contract. The method consists of

dipping the CdS film in a hot (90°C) solution of CuCl for about 5 seconds, rinsing, drying, and then heat treating for about 2 mintues at 250°C.

b. Nonaqueous Barrier Process

The function of the heat treatment process following barrier formation is not at all understood. There has been a suspicion that its main function is to drive off moisture from the barrier surface and that it is only partially effective in doing this. It is well known that moisture lowers the output of CdS solar cells in direct proportion to the amount of moisture present, and that the effect can be reversed by simply removing the moisture. It is possible that the present process does not remove all of the moisture and that better results could be obtained if it did, or if the moisture were never present in the first place.

To check this possibility a barrier plating solution was made up by dissolving cuprous ions in ethylene glycol solvent. Six cells, each 1-1/2" x 1-1/2" in size, were fabricated without the aqueous HCl pre-etch. These cells gave very uniform results with efficiencies between 4.6 and 4.9%. Three cells were then processed using a 3:1 HCl-water solution pre-etch followed by a 5 second dip in the nonaqueous barrier solution. These gave appreciably higher outputs of 6.3, 6.5, and 7.5%.

The cells that were processed without the pre-etch and which were never in contact with water were particularly interesting. These gave unusually high open circuit voltages between 0.53 and 0.55 volts, and showed no drop in output for a period of days. The reason for the higher outputs from the pre-etched cells could be due to the more active surface presented to the chemiplating solution. The benefits of the etched surface might be realized without the presence of water, so that the higher cell voltages could also be obtained. More intensive work along these lines could lead to further cell improvements.

c. Alternate Anions

A number of cells were processed using bromine and iodine in place of chlorine in the pre-etch and in the barrier dipping solutions. The thought was that if chlorine were diffusing into the CdS lattice along with copper, then bromine or iodine would probably be as effective and might also be more stable in the CdS lattice. The cells actually did not appear to be any different as regards stability, but several of these cells gave the highest initial efficiencies yet recorded for CdS solar cells. Three cells, two of which were of 50 cm^2 area, had efficiencies of 8% or more.

Table IV summarizes the initial cell outputs from this series of experiments. The highest output cells were obtained when HBr and HI were used for the pre-etch in place of HCl. This seems to have had more effect than the use of CuBr in the barrier dipping solution. Of course, these are the results of only a few experiments and these very high outputs were not retained for more than a day or so. Yet the high values were very carefully verified and are believed accurate.

TABLE IV

EFFECT OF ANIONS OTHER THAN CHLORINE IN THE PRE-ETCH AND BARRIER DIPPING SOLUTIONS

Pre-Etch	Barrier Dip	Cell No.	Active Area	Initial Cell Efficiency	Remarks
HF	CuCl	D91H4	12 cm^2	2.9%	
HCl	CuCl	D37F4	12	6.7	Std. Process
		D91H1	12	5.8	Std. Process
	CuBr	D37F2	12	7.6	
HBr	CuCl	D37F3	12	8.35	
		D91H2	12	5.2	
		D37C	50	8.0	
		D37D	50	7.8	
		D81G	50	7.0	
	CuBr	D37F1	12	7.0	
HI	CuCl	D83F	50	8.2	
		D91H3	12	5.0	

Figure 9 is the I-V curve for cell D83F which gave the highest output for any 50 cm^2 area CdS film cell measured to date. It was tested in tungsten light equivalent to 100 mW/cm^2 sunlight and gave 0.4 watts maximum power output. The total gridded area was actually 52.1 cm^2. Thus, at short circuit it produced 25.7 mA/cm^2. The fill factor was 66%. If allowance is made for the 15% of the gridded barrier area covered by the grid, the active illuminated barrier produced 30.3 mA/cm^2 short circuit current density and was 9.6% efficient. In extraterrestrial sunlight, this cell would be expected to produce 0.48 watts of power.

Cell No. D37F3 was a smaller cell, 1-1/2" x 1-1/2" in nominal size with a gridded barrier area of 12.1 cm^2. This cell produced 0.101 watts of power in equivalent air mass 1 sunlight with an OCV of 0.490 volts, SCC of 0.295 amperes, fill factor of 69% and conversion efficiency of 8.35%. This is the highest value that has been observed and verified in this laboratory for any CdS solar cell to date. The I-V curve for this cell is shown in Fig. 10. The active illuminated barrier produced at the rate of 9.8% conversion efficiency.

Both of these two highest efficiency CdS film solar cells had the regular Clevite barrier dip process except that the one had a pre-etch in HBr and the other in HI. It appears that the pre-etch should be examined more closely than it has been up to this time.

CELL CONTACTING

a. Pressure Contact Grid

More than 3 years ago conversion efficiencies of 2 to 3% were first obtained from frontwall metal substrate cells as a result of the work of T. A. Griffin[36] in applying a fine mesh metal grid as the contact to the barrier surface. The grids were electroformed, with mesh sizes up to 270 lines per inch, and had light transmissions of 80 to 90%. They were obtained commercially,[37] and the breakthrough in the art of making thin film solar cells consisted of holding such grids in pressure contact to the cell by laminating in plastic.

This method of contacting made possible the transfer of the current generated in the cell to an external circuit with minimal voltage drop. Different grids, plastics and adhesives were evaluated and a process was developed that gave reasonably reproducible results for large area cells. With minor modifications this process[38] has been used for most of the frontwall cell contacting of the present contract.

The method consists of laying up, in order: a 1 or 2 mil thick film of Mylar or Kapton plastic, a 1/2 mil thick film of Capran (nylon) plastic, a negative lead of silver foil, a thin film CdS cell with barrier surface up, insulating plastic strips where the leads cross the edges of the cell, an electroformed metal mesh grid, a positive lead of silver foil, a 1/2 mil thick Capran plastic film, and an upper 1 or 2 mil thick film of

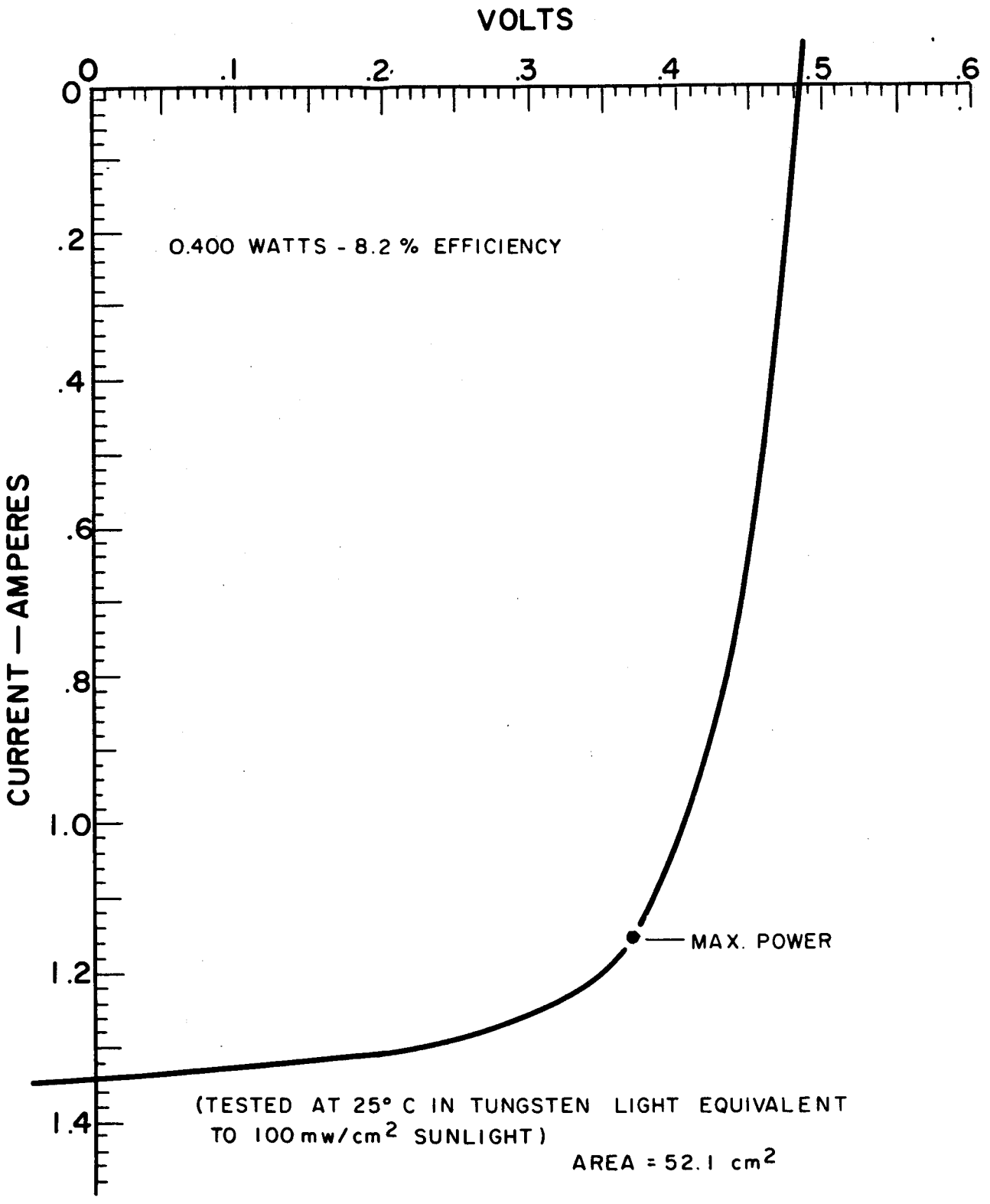


FIG. 9. I-V CHARACTERISTIC CURVE OF HIGHEST OUTPUT 3" x 3" CdS FILM CELL

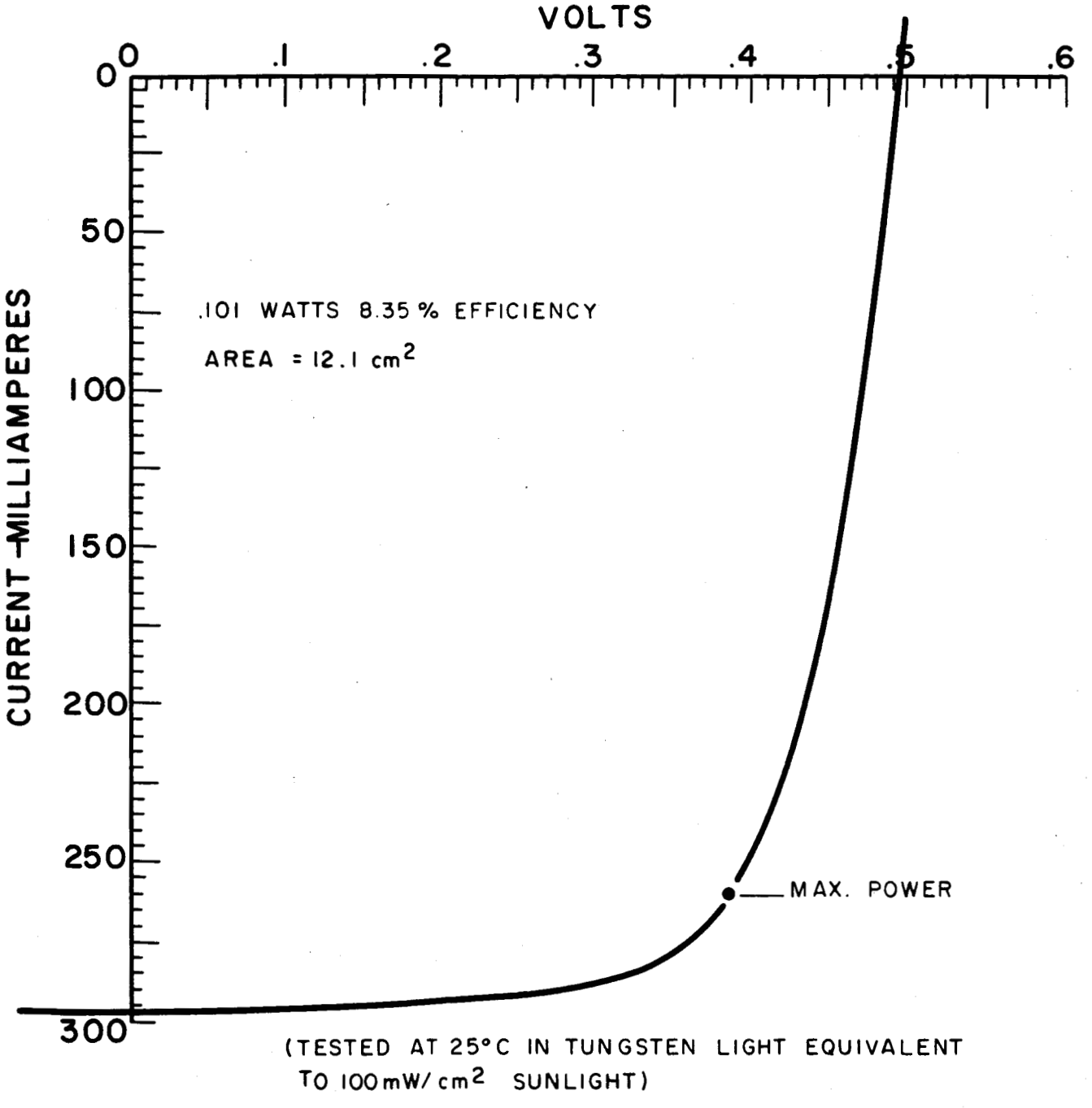


FIG. 10. I-V CHARACTERISTIC CURVE OF HIGHEST OUTPUT CdS SOLAR CELL

effect, this is just what is being used for the grids of recent CdTe thin film solar cells.[40, 41] But these cells are apparently series resistance limited even with these design provisions when tested at sunlight levels of 80 mW/cm^2. At higher light levels the series resistance effect should be even more severe.[42]

2. Electroplated Grids

Unidirectional copper and silver grids were electroplated onto the barriers of high efficiency frontwall metal substrate film solar cells. These made good low resistance contacts and had low lateral resistance. Though a number of different electroplating baths were tried, however, in every case the electroplating operation was very harmful to the output of the cell. Others[43] have had similar difficulties with electroplated grids on CdS film cells. They have managed to secure operable cells with electroplated grids by resort to photo resist masking techniques. Even though such cells were relatively low in output they did stand up on vacuum thermal cycling.[44]

3. Cemented Grids

In this laboratory a technique was developed to cement the metal mesh grids to cell barriers using conducting epoxy silver compositions. Two methods of applying the cement to the grids were evaluated: transferring from an inked plate, and spraying from a thinned solution. Best results as far as cell performance was concerned were obtained by the transfer method, though the spray technique was more convenient and gave a neater appearing cell.

The technique used for the transfer method is to spread out an even thin layer of epoxy cement[45] on a flat glass plate using a roller or squeegee. The metal mesh grid is then placed down onto this layer of cement with an even rolling motion, permitted to sink in slightly, and then peeled off and placed on the barrier of the cell to be contacted. The epoxy is cured with a flat weight pressing the grid lightly against the barrier.

This method was developed using small area cells at first until the operators acquired the necessary dexterity and were able to secure cells of better than 4% conversion efficiency with little spreading or smearing of the epoxy cement. Then, larger cells, of the 3" x 3" size were fabricated with these cemented grids. On these there was some slight spreading of the cement with a consequent loss in the illuminated area of the cells, but the cell efficiencies were only slightly below the level experienced at the time with pressure contact grids.

Table V lists the first 9 large area cells contacted by this method. These averaged 4. 1%, ranging between 3. 6 and 4. 9%, in efficiency. They were delivered to the Lewis Research Center, NASA, for evaluation and vacuum thermal cycling test.[44] They all dropped in output to less than 25% of their initial value in the first 100 temperature cycles, and then

TABLE V

OUTPUT OF EARLY FRONTWALL METAL SUBSTRATE CELLS WITH CONDUCTIVE EPOXY CEMENTED GRIDS

Cell No.	Area cm^2	OCV V	J mA/cm^2	Max. Power Watts	Eff. %	Remarks
315D	48.9	.45	14.6	.204	4.9	
320D	48.3	.415	15.9	.191	4.0	
331A	49.3	.445	15.6	.221	4.5	
331D	48.3	.415	16.2	.180	3.7	
333A	47.5	.46	15.7	.209	4.4	
336B	48.6	.43	14.5	.189	3.9	Gold Grid
337B	48.3	.43	15.9	.189	3.9	
337C	46.8	.45	12.5	.172	3.7	Gold Grid
339B	48.6	.425	14.7	.176	3.6	Gold Grid
Avg.	48.3	.436	15.1	.192	4.1	

Notes:

60 lpi electroformed grids -- copper unless otherwise noted.
Tested in tungsten light equivalent to 100 mW/cm^2 sunlight.
No. 3021 conductive silver epoxy composition used as cement.

levelled off and showed no further drop (as of 1500 cycles). There was no indication of any short circuits occurring which had been the weakness of the cells with pressure contact grids.

One of these cells, which was originally 3. 9% efficient, was returned to our laboratory after degradation on the NASA temperature cycling test and found to be still 3. 4% efficient on our test. On further investigation it was discovered that these epoxy compositions do not make a good permanent bond to copper (and possibly to certain other metals). Grids that had been so cemented could be peeled off intact from the cement after the epoxy had been fully cured.

This action could explain the steady degradation of these cells on thermal cycling. It was found that the nonadherence of the cement to the grids could be solved by first silver plating the grids.

Table VI lists a second group of 3" x 3" cells whose grids were first silver plated and then cemented in place with conducting epoxy. These cells were also furnished to the Lewis Research Center, NASA, for evaluation. It is understood that some of these have also shown a steady degradation of output on thermal cycling, but there has not been time to analyze the data or the cells.

c. Etched Grids

The electroformed metal mesh grids are delicate to handle, very expensive, and have been difficult to secure to the desired thickness tolerance. Therefore, attempts were made to secure similar grids made by a photoetching process.

A special grid pattern was designed for a standard 3" x 3" size cell having 60 wires per inch in one direction and 10 per inch in the perpendicular direction. The 60 per inch wires are the main current carrying wires and are tapered from about 3/4 mil wide at one end to about 1-1/4 mils wide at the other end where there is an integral tab extending 1/2 inch the full width of the cell to act as the positive lead. There is a 14 mil wide border around the other 3 edges for improved handling and physical rigidity of the grid. There are 10 evenly spaced holes on the tab which could be used for a bolted or riveted connection, but which are primarily intended as locating holes for the fixturing in fabricating the cells.

Some difficulties were experienced by the vendor[46] in fabricating these grids, but revisions in the process have been made and it now appears that these grids can be supplied satisfactorily on an economic basis. A number of cells have been fabricated using these grids, both with the pressure contact method and the cemented grid method, and they are far more convenient to handle than the electroformed grids.

There have not been sufficient cells made with the etched grids on a controlled experiment basis to determine whether the revised geometry and other features are really beneficial or not, and no stability data are

TABLE VI

OUTPUT OF FRONTWALL METAL SUBSTRATE CELLS WITH CONDUCTIVE EPOXY CEMENTED SILVER PLATED COPPER GRIDS

Cell No.	OCV	SCC	J	Max. Power	Fill	Eff.	Age	Highest Initial Eff.
	V	A	mA/cm^2	W	%	%	Days	%
D40D	.475	.750	15.0	.242	69	4.9	21	5.1
D40H	.480	.715	14.3	.233	67	4.6	21	4.8
D39D	.485	.720	14.4	.202	58	4.0	63	5.2
D60H	.468	.783	15.6	.241	66	4.8	43	4.9
D63H	.465	.820	16.4	.246	65	4.9	48	5.2
D64F	.455	.720	14.4	.202	62	4.0	43	4.2
D84G	.465	.810	16.2	.226	60	4.6	36	5.5
Avg.	.470	.760	15.2	.227	64	4.54	39	4.99

Notes:
60 lpi electroformed copper grids.
Cemented with No. 3021 conductive epoxy.
Tested in tungsten light equivalent to 100 mW/cm^2 sunlight.
All cells 50.0 cm^2 area.

available as of this writing. Cell efficiencies have varied from about 5% up to as high as 7. 1% for 3" x 3" cells.

Figure 11 shows the use of an etched grid on a cell. This is a photograph of a copper substrate 3" x 3" cell with an integral extension of the substrate at one edge acting as the negative lead of the cell, and an etched grid cemented in place with conductive epoxy cement with the integral extension of the grid at the opposite edge of the cell acting as the positive lead. The cell is encapsulated with Mylar using Capran adhesive.

d. Lamination Process

Recent data points to the lamination process as a major factor affecting both cell output and stability. Photomicrographs taken of the cross-section of finished cells with pressure grid contacts disclosed that Capran plastic frequently flowed between the grid and the cell barrier. At first this was thought to result from lack of control of the thickness of the grid relative to the thickness of the Capran layer. Excess Capran would allow the grid to float away from intimate contact to the barrier.

However, when thickness control was established, evidence of Capran beneath the grids continued. It is now evident that when the Capran melts during lamination it wets the grid and the cell barrier and runs in between by capillary action. This effectively reduces the area of the grid contact, increases series resistance, and reduces short circuit current and cell efficiency.

In order to alleviate this condition, laminations were carried out at lower temperatures in hopes that the Capran would be more viscous and thus have less tendency to run beneath the grids. This was tried first on small area cells and a dramatic increase in cell output was obtained as the lamination temperature was reduced. There was a limit in how far this could be carried because beyond a certain point the cells would not be completely laminated. Incomplete lamination shows up first by poor optical coupling between cell and plastic, and then by the package coming apart.

It was found that only a few degrees separated the extremes of over lamination and underlamination. This working region was then evaluated with large area cells. The results are summarized in Table VII.

As the lamination temperature was reduced from 235° to 228°C to 224°C there was a regular decrease in series resistance which resulted in a marked increase in fill factor and efficiency.

Unfortunately, these very high initial efficiencies were not retained for more than a day or so, but fell off relatively rapidly for a few days, and then more slowly after that. It appeared that the lower lamination temperatures which gave more area of grid contact, also caused the grids to be held less firmly so that the pressure contact gradually relaxed.

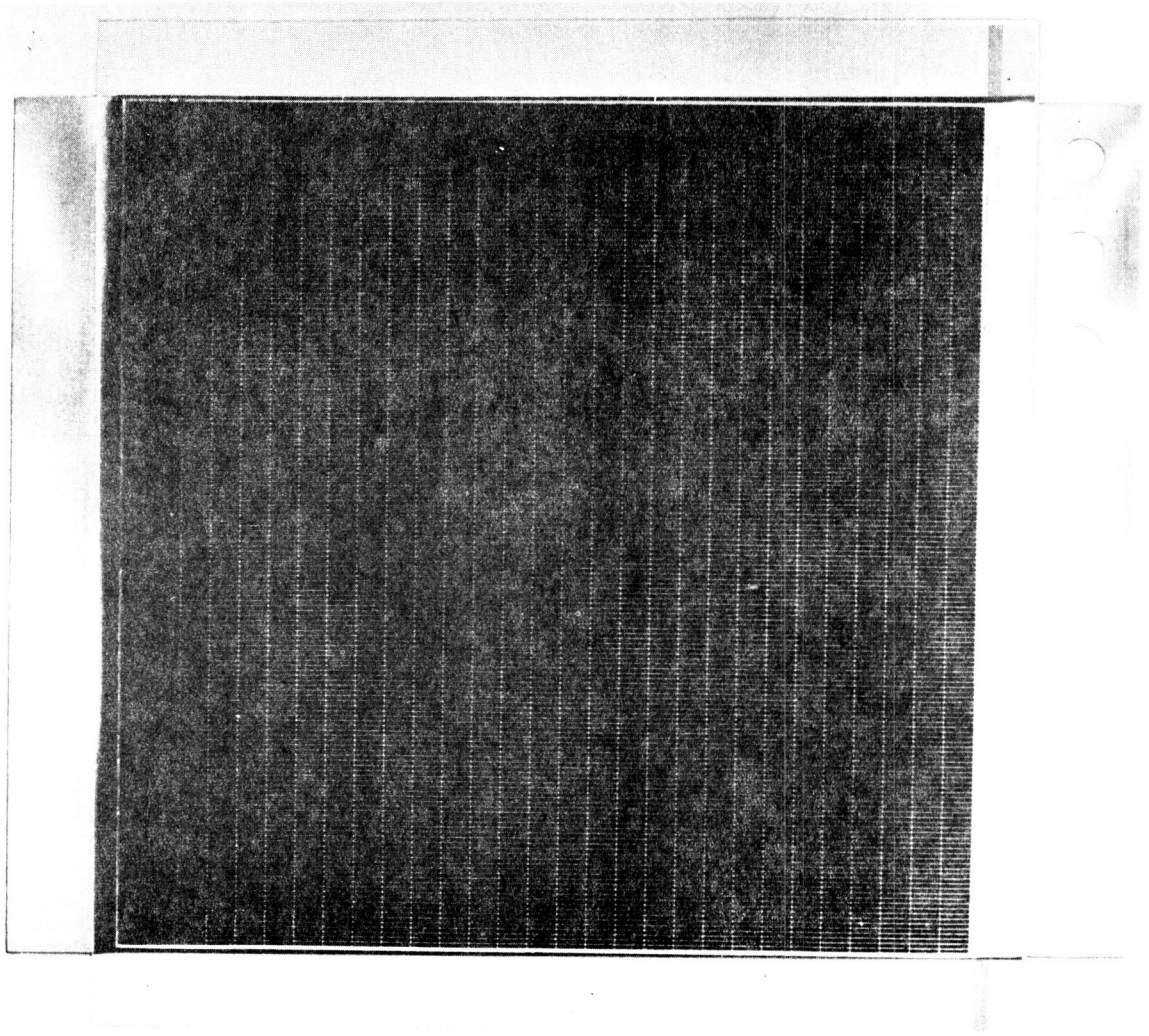


FIGURE 11: 3" x 3" COPPER SUBSTRATE CELL WITH ETCHED COPPER CEMENTED GRID AND INTEGRAL LEADS

TABLE V II

EFFECT OF LAMINATION TEMPERATURE ON CELL OUTPUT

Lamination Temp. & Time °C	min	Cell No.	OCV v	J (mA/cm^2)	R_S ohms	Fill (%)	Eff. (%)
235	4	D41E	0.48	18.8	0.10	57	5.4
		D41F	0.47	18.8	0.11	54	4.8
		D50A	0.48	20.6	0.10	55	5.5
		D50E	0.46	20.9	0.10	52.5	5.3
		Avg.	0.47	19.8	0.103	55	5.25
228	15	D46D	0.47	19.7	0.09	58	5.9
		D46F	0.47	19.3	0.08	64	5.8
		Avg.	0.47	19.4	0.085	61	5.85
224	15	D51B	0.47	22.4	0.05	70	7.2
		D51D	0.47	23.1	0.05	68	7.4
		D51E	0.47	24.0	0.05	70	7.8
		D51H	0.47	21.5	0.05	68.5	7.0
		Avg.	0.47	22.8	0.050	69	7.35
224	20	D38C	0.47	20.2	0.06	67	6.5
		D38H	0.48	22.0	0.05	68	7.2
		D39C	0.47	20.5	0.07	67	6.4
		D39H	0.47	20.5	0.07	65	6.2
		Avg.	0.47	20.3	0.063	67	6.58

Notes:

All cells 50 cm^2 area, 0.002" thick molybdenum substrates, 20μ thick CdS, encapsulated in 0.002" thick "Mylar" using 0.0005" thick "Capran" adhesive, and 60 lpi copper mesh grids.

This experience was important in bringing attention to the fact that the barrier of the CdS solar cell is at least initially inherently a 6 to 8% device as fabricated by the present process, and also that a major factor in cell instability in the past has been a relaxation of the grid contact.

Following this series of experiments, the temperature of lamination for pressure grid contact cells was increased to 233°C to favor the better cell stability over the higher initial outputs. This has demonstrated clearly that a better method of cell contacting is required.

CELL TESTING

a. Output Testing

The cells are tested for output by holding them on a temperature controlled block, illuminating them with a calibrated light, using a variable load and plotting the I-V characteristic curve with an X-Y plotter.

Temperature control is maintained by vacuum hold down onto a perforated heavy brass block the temperature of which is held at 25°C ± 0. 5°C by a built in thermoelectric cooling unit and a resistance type heater.

Illumination is by a tungsten lamp[47] operated at an overvoltage of 135 volts to give a color temperature of about 3800°K. A water filter is used. The light level is measured with a thermopile and adjusted by changing the distance between the cell and the light source.

The light level is calibrated by measuring a large number of similar construction cells of known good stability in direct sunlight of 80 mW/cm^2 intensity or better, and extrapolating the curves obtained to 100 mW/cm^2 intensity level. The cells are then placed in the tungsten light and the source to cell distance adjusted to yield the same output (efficiency and short circuit current). The absolute light level as indicated by the thermopile is recorded in each case. The average of these readings is then used to adjust the light level for subsequent tests. Calibration is carried out at irregular intervals. Calibration checks using secondary standards are carried out at regular intervals.

Contacts are made to the solar cell by separate load and voltage leads. The load is carried by large area clamping contacts while cell voltage is read through noninteracting small area contacts. These precautions are very important for large area solar cells which generate an ampere or more of current.

Load is placed on the solar cell by a variable voltage supply. The I-V curve is drawn in the fourth quadrant and is extended slightly into the first and third quadrants. In all cases the light is turned on about 100 seconds prior to tracing the curve to ensure equilibrium conditions. Some cells show a hysteresis effect which has been found to be transient and to disappear after a short period of constant illumination.

This method has been reasonably satisfactory for testing large area thin film CdS solar cells at the present state of development. The absolute accuracy of the test method is probably well within ± 5% and the relative accuracy within ± 1%. Other laboratories check our results closely. Improvements to yield higher accuracy and greater convenience are planned however.

b. Temperature Performance

The temperature performance of a large area plastic substrate cell is shown in Fig. 12. The I-V curve at 10°C temperature intervals from 10°C to 100°C was taken for a representative 50 cm^2 area 5% efficient cell. The drop in efficiency, OCV and SCC was almost exactly linear with temperature over this range as can be seen in Fig. 13. It is interesting that there was also a steady drop in the fill factor from 71% at 10°C to 62% at 100°C.

This regular pattern is somewhat different than has been observed on earlier[4,48] lower efficiency cells of the frontwall metal substrate construction. Earlier, the current was observed to rise with increasing temperature, level out and then fall. This gave somewhat of an "S" shape to the temperature-efficiency curve.

A number of frontwall metal substrate cells were also tested for output over this temperature range. Cells of 5% conversion efficiency generally confirmed the pattern shown in Figs. 12 and 13, while lower efficiency cells gave results more like the earlier data. These data are still preliminary and more extensive tests over wider temperature ranges are needed.

c. Spectral Response

An experiment was run to determine whether there was a shift in the spectral response of CdS film cells as they degraded due to moisture exposure. A molybdenum substrate cell, 1-1/2" x 1-1/2" in size with a gold grid held in pressure contact by the Mylar-nylon encapsulation was chosen for the test. The cell was initially 6. 7% efficient. The spectral response was taken using a Bausch and Lomb diffraction grating monochrometer with the slits open to 5 mm. A white light bias was used and the output from the white light bias was subtracted from each reading. The cell output was taken across a 100 ohm resistive load (close to open circuit conditions). The readings were normalized to constant light input energy at each wavelength. A filter was inserted at wavelengths greater than 700 mμ to remove second order effects from the instrument.

The tungsten lamp used did not permit measurements below 400 mμ. Appreciable response was obtained at 500 mμ, there was a broad peak between about 400 and 750 mμ, and a final cut-off between 1050 and 1100 mμ. The upper curve of Fig. 14 represents the response initially, before degradation.

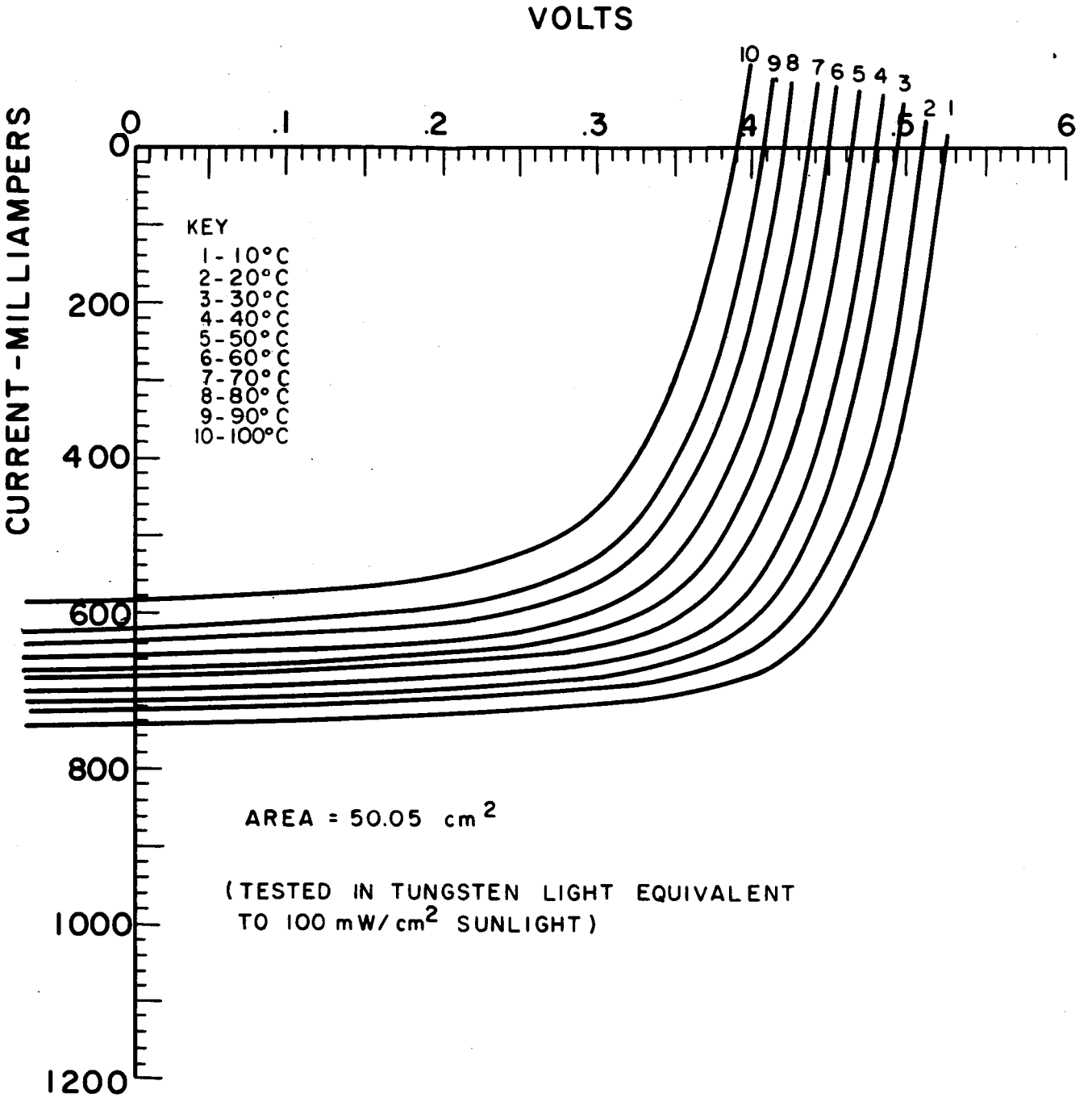


FIG. 12. I-V CURVES OF 5% LARGE AREA CdS CELL AT VARIOUS TEMPERATURES FROM 10° C TO 100° C

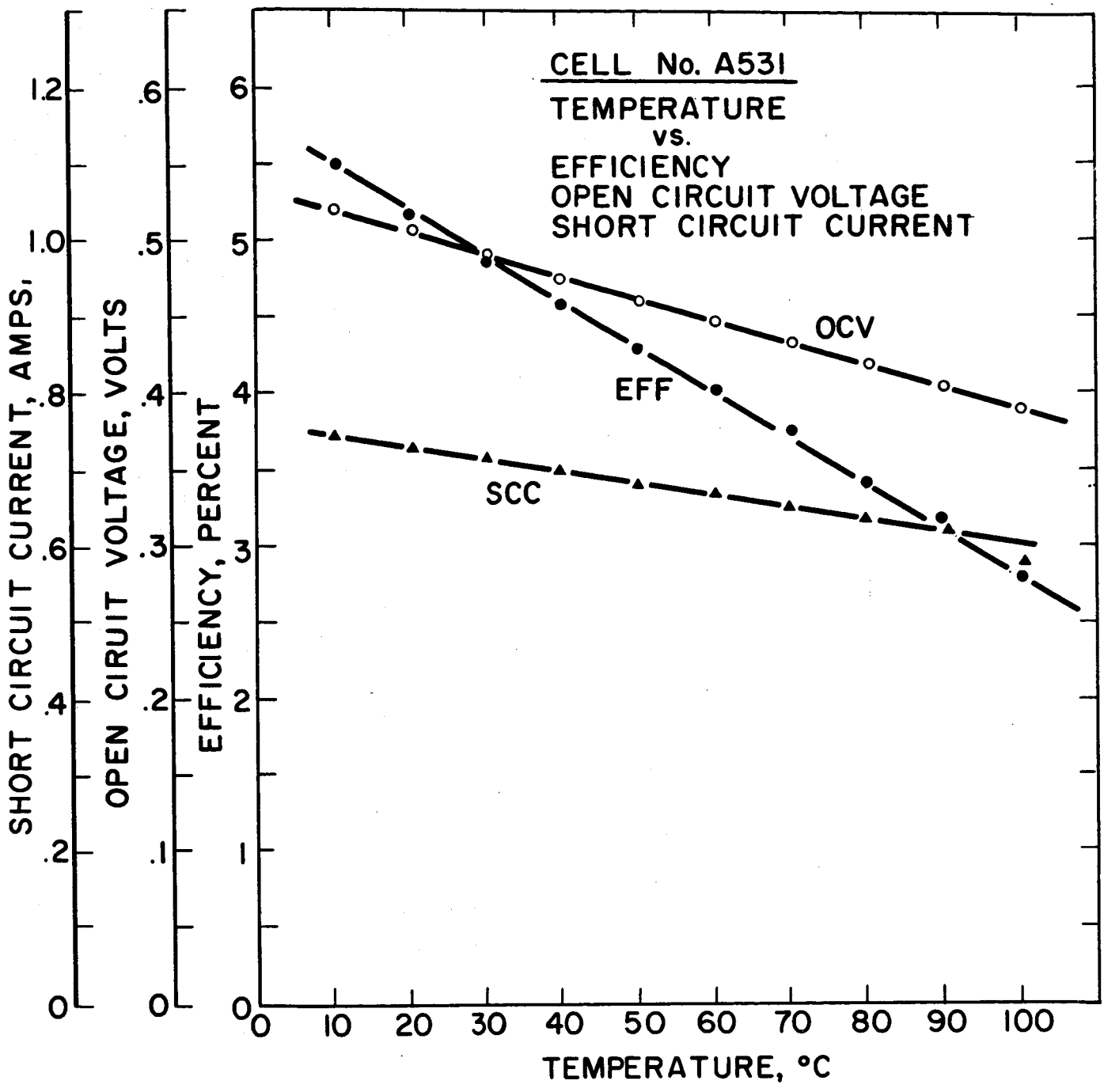


FIG. 13. TEMPERATURE PERFORMANCE OF 5% PLASTIC SUBSTRATE CELL

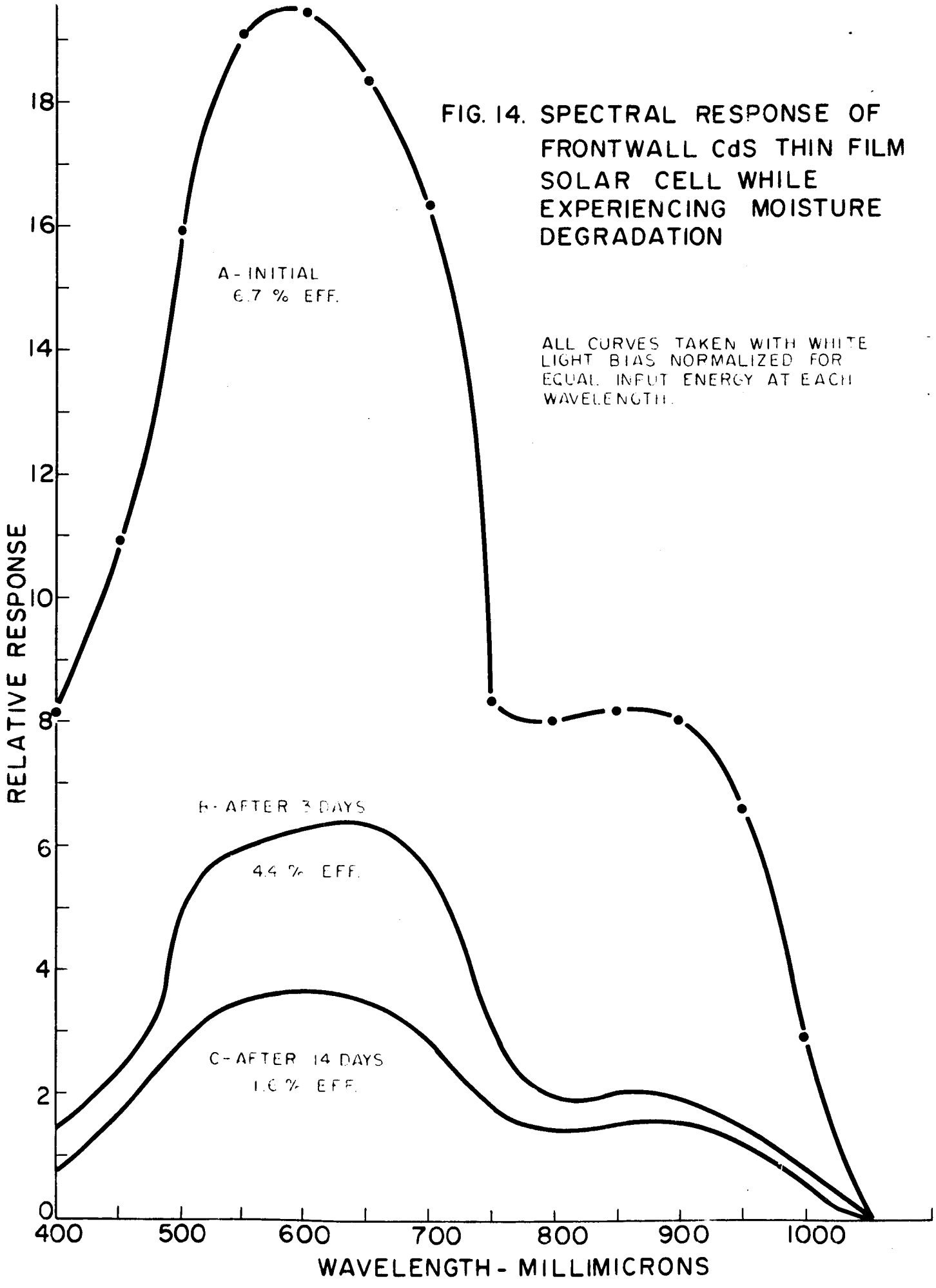


FIG. 14. SPECTRAL RESPONSE OF FRONTWALL CdS THIN FILM SOLAR CELL WHILE EXPERIENCING MOISTURE DEGRADATION

ALL CURVES TAKEN WITH WHITE LIGHT BIAS NORMALIZED FOR EQUAL INPUT ENERGY AT EACH WAVELENGTH.

ERD 5040

The cell was left out in high room humidities for 3 days and measured again. It had degraded to 4. 4%. The spectral response of the cell at 4. 4% had the same shape but gave lower values at each wavelength, as can be seen by the second curve of Fig. 14.

After another 10 days room storage at high humidities the cell had degraded to 1. 6% and again the spectral response was the same except that it was lower at all wavelengths. Thus the degradation, presumed due to moisture exposure, appears to be spectrally nonselective.

In Fig. 15 the spectral response of another cell of the molybdenum substrate Mylar encapsulated gold grid construction is presented. This also was a 1-1/2" x 1-1/2" size cell, fully illuminated. The cell was 5. 0% efficient. However, for this measurement the slits of the monochromator were narrowed to 1 mm opening to sharpen the resolution (dispersion was 33 A). Here both the monochromatic response and the response under bias light (with the bias light response subtracted at each reading) are plotted. A very sharp peak was obtained at 500 mμ representing the intrinsic response of the CdS. Surprisingly, the white light bias seems to have given tremendous enhancement of this intrinsic response.

This curve is also notable for a quenching effect at long wavelengths. At greater than 670 mμ there was less output under bias conditions than there was without bias light. This appears to be analogous to infrared quenching of photoconductivity in CdS. It is presumably caused by certain types of impurities or native defects in the CdS. It is not known whether these are the same impurities or defects which give rise to the large enhancement in the green and blue regions.

Figure 16 illustrates a different spectral response pattern for a CdS thin film solar cell. The cell was made from a CdS film that was evaporated with a trace (approximately 5 ppm) of copper as CuCl added to the charge. The copper counterdoping was not sufficient to make the CdS insulating however, only about enough to increase the bulk resistivity by 1 to 2 orders of magnitude. The cell was 4. 0% efficient. The response was taken with the slits open at 5 mm, on a 3" x 3" cell with all but 1-1/2" x 1-1/2" of the area masked. It is interesting that enhancement was obtained at all wavelengths and that considerable structure is evident between 500 and 700 mμ for both curves.

STABILITY STUDIES

a. Shelf Stability

1. Long Term Stability - (1 Year)

Some of the first high efficiency frontwall metal substrate cells fabricated by the revised Clevite process over a year ago are still performing at the same level. These were Mylar encapsulated cells with

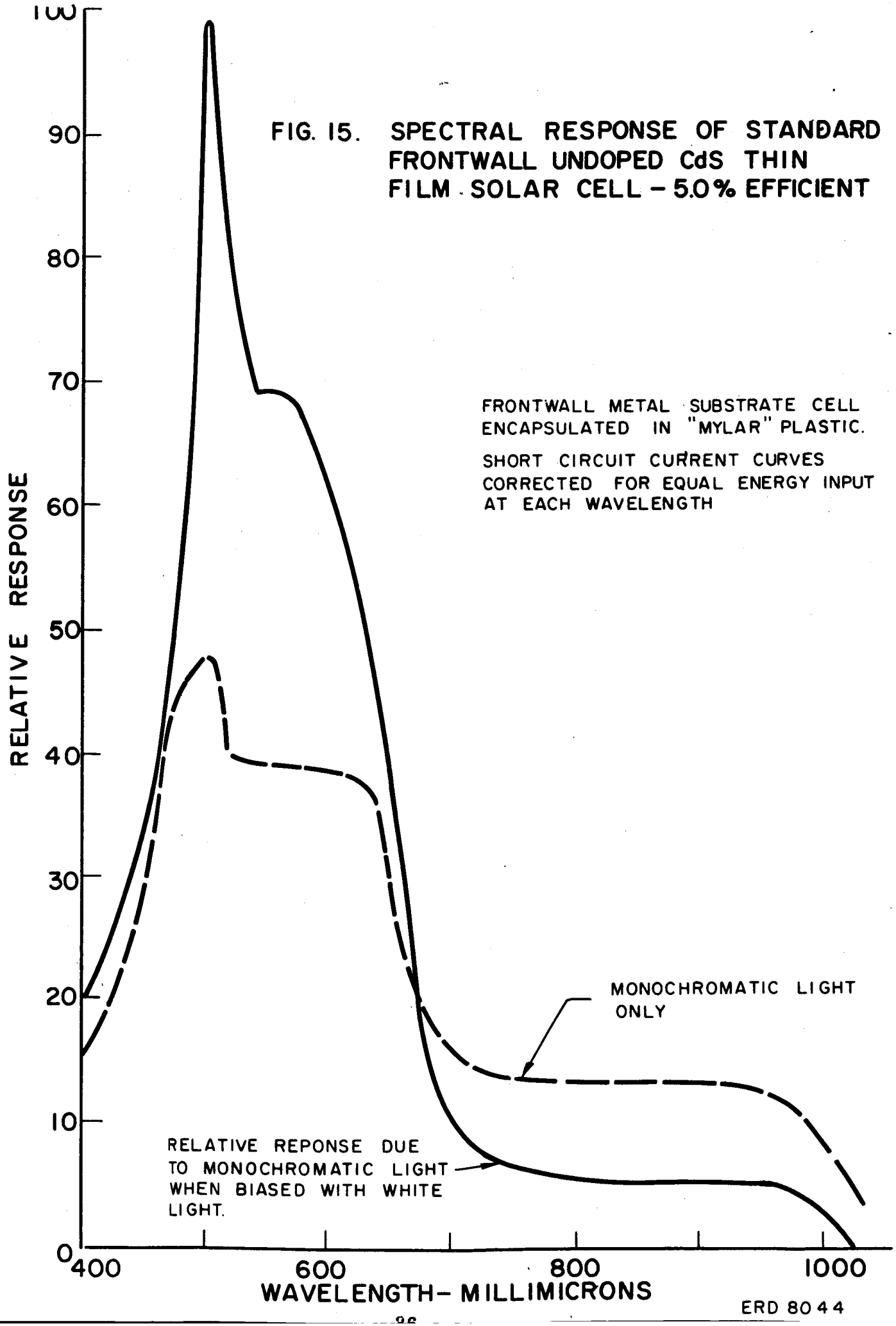


FIG. 15. SPECTRAL RESPONSE OF STANDARD FRONTWALL UNDOPED CdS THIN FILM SOLAR CELL – 5.0% EFFICIENT
FRONTWALL METAL SUBSTRATE CELL ENCAPSULATED IN "MYLAR" PLASTIC.
SHORT CIRCUIT CURRENT CURVES CORRECTED FOR EQUAL ENERGY INPUT AT EACH WAVELENGTH
RELATIVE RESPONSE
100
90
80
70
60
50
40
30
20
10
0
400
600
800
1000
WAVELENGTH – MILLIMICRONS
MONOCHROMATIC LIGHT ONLY
RELATIVE REPONSE DUE TO MONOCHROMATIC LIGHT WHEN BIASED WITH WHITE LIGHT.
ERD 8044

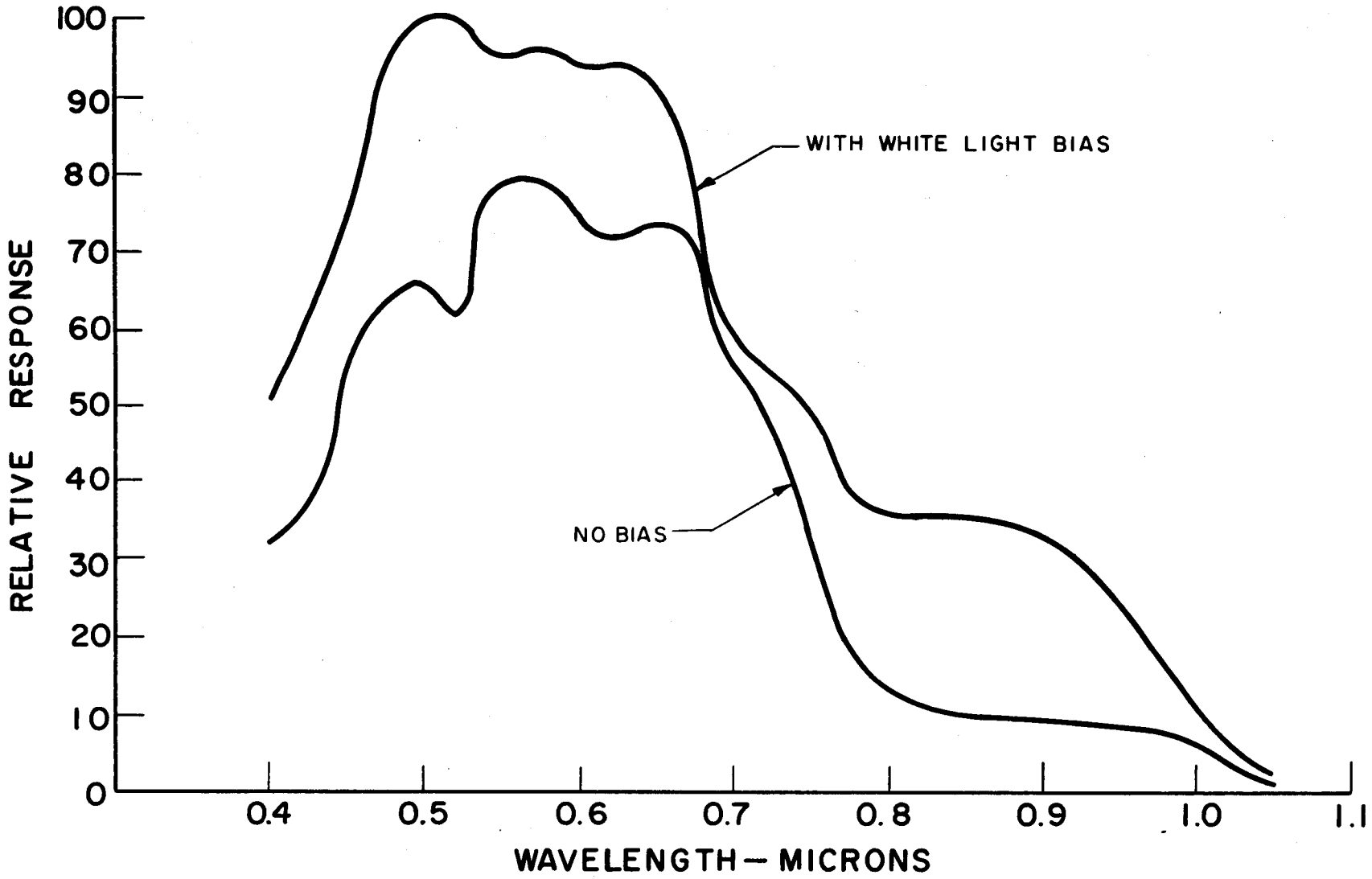


FIG. 16. SPECTRAL RESPONSE OF FRONTWALL COPPER-DOPED CdS THIN FILM SOLAR CELL

electroformed gold grids held in pressure contact to the barrier with Capran adhesive. Table VIII lists the data on three of these early cells which are still on dry shelf storage in our laboratory.

Cell No. 73C has been kept in a desiccator except for short periods of testing in room ambients. Cells 205 and 213 were sent to NASA, Lewis Research Center, given 2920 cycles on their vacuum thermal cycling test, then returned and kept in a desiccator, except for short periods of testing in room ambients. It is evident that these cells are not undergoing noticeable degradation.

Other cells of this construction that were submitted to NASA, Lewis Research Center, and to the Air Force Aero Propulsion Laboratory, have been equally stable. Thus some CdS thin film solar cells, even with pressure grid contacts, have been stable at the 4 to 5% conversion efficiency level for periods of at least a year.

2. Intermediate Term Stability (3 to 6 Months)

There have been widely differing experiences on newer design CdS thin film cells on desiccated shelf storage for intermediate periods of time. Table IX lists a dozen of the first high efficiency large area frontwall plastic substrate cells that were made about 6 months ago. Most of these cells showed some drop in output after reaching an initial peak. Subsequently some rose in output while others held steady. There are differences in behavior between individual cells and it is difficult to determine how much of this can be ascribed to the test. There is a hint in the data of some of these cells that the pressure exerted by the grid contact might be varying slightly from time to time. On the average, this group of cells taken as a whole, does appear to be reasonably stable.

Similar data are presented in Table X for frontwall metal substrate cells that were made about 5 months ago. These are exhibiting a definite, though small, continuing degradation of output after the initial drop of the first few weeks.

Table XI presents similar data for a group of frontwall metal substrate cells that were made about 3-1/2 months ago, with what were presumed to be the same conditions. Here, there is also a definite trend. There is a drop of about 10% in output in the first two weeks followed by a slow drop in succeeding periods.

It is believed that this slow degradation is due to a relaxation of the pressure contact grid, and that the cells showing this slow degradation were probably laminated at slightly lower temperatures than cells not showing the slow degradation -- though the conditions were presumed to be the same at the time they were laminated. This belief is substantiated by the experience that cells that have degraded like those of Table XI can usually be restored to their original output, or close to it, by a simple relamination. As shown by the data in Table VII, a rise in initial output

TABLE VIII

LONG TERM SHELF STABILITY OF EARLY HIGH OUTPUT CdS THIN FILM SOLAR CELLS

Cell No.	Area	Initial Efficiency	Present Efficiency	Age
73C	4.3 cm^2	4.8%	4.8%	14-1/2 months
205	49.0	4.2	4.1	11-1/2
213	46.8	4.2	4.2	11-1/2

Notes:
Frontwall molybdenum substrate cells with 60 lpi gold grids held in pressure contact by Mylar encapsulation using Capran adhesive.

TABLE IX

SHELF STABILITY OF EARLY LARGE AREA FRONTWALL PLASTIC SUBSTRATE CdS THIN FILM SOLAR CELLS

Cell No.	Conversion Efficiency at: Initial	1/2 Mo.	1 Mo.	2 Mos.	3 Mos.	4 Mos.	6 Mos.
A490	5.3%	3.6%	3.7%	3.6%	4.3%	4.3%	4.1%
A491	4.0	3.1	3.5	3.5	3.8	3.7	3.6
A497	5.0	4.2	5.0	4.8	5.5	5.5	5.1
A500	5.7	5.0	5.3	5.0	5.7	5.7	5.8
A513	4.6	4.7	4.8	5.2	5.2	5.0	5.0
A531	5.2	4.7	5.0	5.3	5.2	5.2	5.0
A538	5.8	5.4	5.4	5.6	5.6	5.7	5.4
A550	5.4	5.6	6.2	6.2	6.2	6.2	6.0
A552	5.0	4.6	4.4	4.9	4.9	4.9	4.6
A554	5.2	4.7	4.5	5.3	5.3	5.2	5.0
A565	4.7	4.6	4.6	5.0	5.0	5.0	5.0
A568	5.4	4.5	4.5	4.8	4.6	4.6	4.3
Avg.	5.1	4.6	4.7	4.9	5.1	5.1	4.9

Note:
Frontwall Kapton plastic substrate cells, gold grids held in pressure contact with Mylar encapsulation using Capran adhesive.

TABLE X

SHELF STABILITY OF LATER LARGE AREA FRONTWALL METAL SUBSTRATE CdS THIN FILM SOLAR CELLS

Cell No.	Conversion Efficiency at: Initial	1/2 Mo.	1 Month	2 Months	3 Months	5 Months
D16B	5.2%	5.0%	4.5%	4.7%	4.7%	4.5%
D16E	4.7	--	--	4.4	4.3	3.9
D18E	5.3	5.0	5.1	4.8	4.7	4.3
D19A	5.3	4.7	4.7	4.7	4.6	4.4
D19F	5.4	5.3	5.0	5.0	4.9	4.6
D21B	5.5	4.7	--	4.7	--	4.4
D21F	4.7	4.4	4.4	4.4	4.4	4.2
Avg.	5.16	4.81	4.70	4.67	4.60	4.33

Notes:

Frontwall molybdenum substrate cells, copper grids, encapsulated in Mylar with Capran adhesive.

In computing averages, missing data points were interpolated.

TABLE XI

SHELF STABILITY OF SOME MORE RECENT LARGE AREA FRONTWALL METAL SUBSTRATE CdS THIN FILM SOLAR CELLS

Cell No.	Conversion Efficiency at: Initial	1/2 Mo.	1 Mo.	1-1/2 Mos.	2 Mos.	2-1/2 Mos.	3-1/2 Mos.
D56A	6.5%	5.7%	5.4%	5.3%	5.2%	5.1%	5.0%
D56B	5.7	5.7	5.4	5.2	5.1	5.0	4.8
D57A	6.1	5.6	5.2	5.1	5.0	4.9	5.0
D58A	6.4	5.8	5.4	5.3	5.2	5.0	4.9
D60A	6.4	5.4	5.2	5.0	4.8	4.7	4.8
D60E	6.5	5.5	5.3	5.1	5.1	5.0	4.9
D62D	5.4	4.8	4.5	4.5	5.1	--	4.0
D62G	6.7	5.6	5.3	5.0	5.1	4.9	4.8
Avg.	6.2	5.5	5.2	5.1	5.0	4.84	4.78

Note:

Frontwall molybdenum substrate cells, copper grids, encapsulated in Mylar with Capran adhesive.

does result from lowering the lamination temperature. Those cells laminated at still lower temperatures showed a still more rapid drop in output than those listed in Table XI.

3. Short Term Stability (< 1 Month)

There have been widely varying changes in the outputs of cells fabricated in different ways in the first few hours, days, or even weeks after cell lamination. The changes are associated with the lamination process rather than with other steps in cell fabrication, because after the output has stabilized the same patterns can be repeated by relaminating cells.

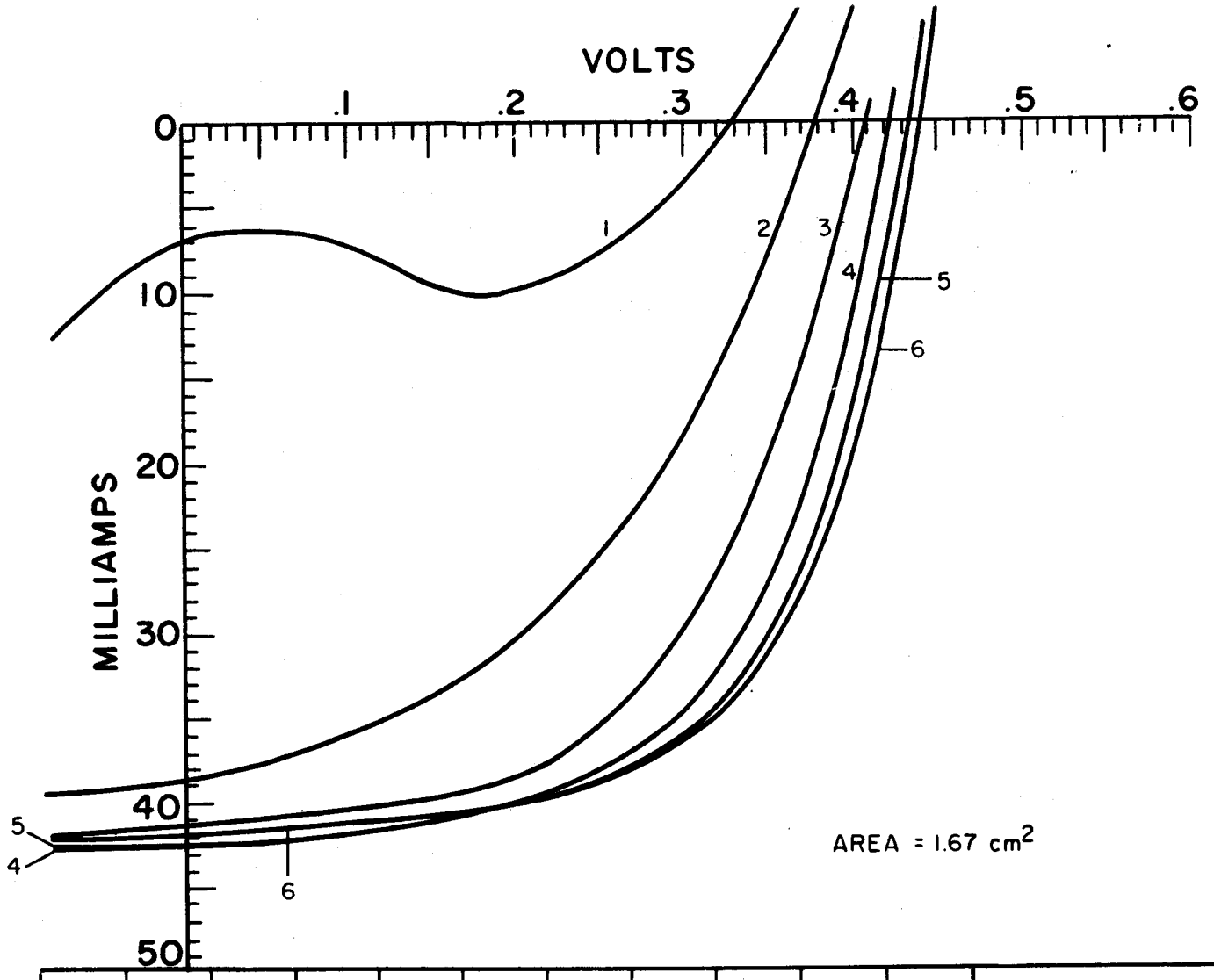
We have tentatively ascribed these "transient" effects as being caused by a relaxation of stresses built in to the package during lamination. They vary somewhat with the type of lamination plastics, temperatures and pressures, and even with the type of cell substrate employed. However, widest variations result from the material of the current collecting grid used as a barrier contact.

Thus, with electroformed gold grids these transient effects are essentially nonexistent and full cell output is obtained immediately after lamination. With electroformed copper grids however, very poor outputs are obtained immediately after lamination with even a double inflection occurring in the I-V characteristic curve as shown by curve 1 of Fig. 17. After a few hours, or in some cases a few days, the voltage and current have both increased and the curve has assumed a rectangular characteristic as illustrated by curve 2. Further improvement in the curve may occur in the next few hours or days, as shown by curves 3, 4, 5, and 6.

Silver grids are somewhat intermediate in this respect with the cells coming up to full output more quickly than cells with copper grids, but less quickly than cells with gold grids. Cells with nickel grids on the other hand are very much slower than copper, and in our experience never quite make the grade though the curves do keep improving for weeks after fabrication.

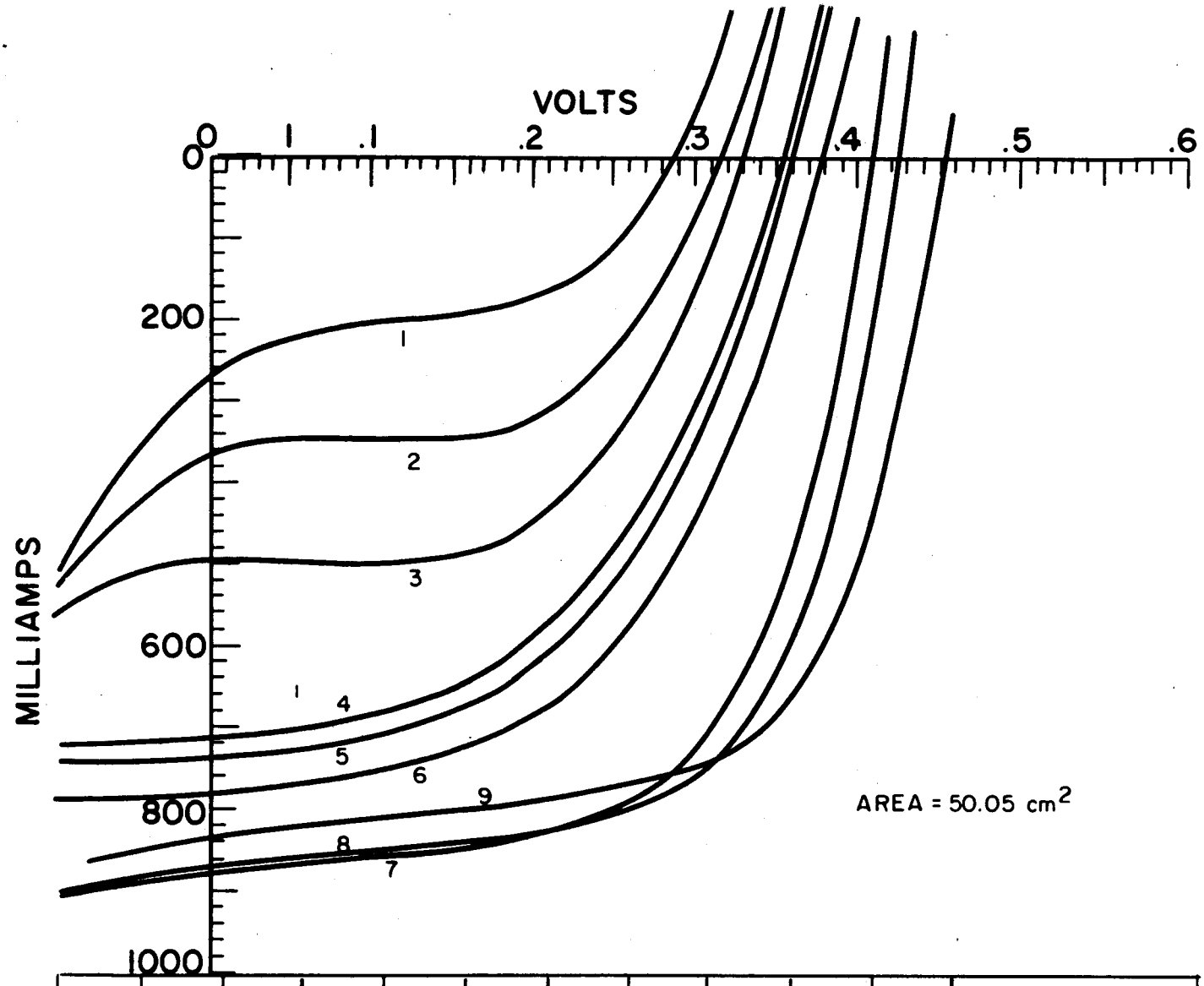
The effect appears to be due to the bulk properties of the grids and not to the surface contact made to the cell barrier. When nickel grids were gold plated and fabricated into cells they behaved like nickel gridded cells, not like gold gridded cells.

Similar effects have been observed for cells with grids cemented in place with conductive epoxy cement. There are wide variations in the pattern depending on the particular epoxy composition used. With one type of cement,[49] the cells initially give outputs of 2 to 3% or less with low open circuit voltages, and these climb very slowly, over a period of weeks or more, without quite reaching the voltage or power output levels obtained with other cements.[45] The pattern is illustrated in Fig. 18.



TEST No.	DATE	TIME	OCV	SCC	SERIES Ω	SHUNT Ω	SCC cm²	MAX WATTS	% - FILL	% EFF	REMARKS
1	11/10/65	1242	.325	7.0						<2.0	
2	"	1312	.378	38.7					43	3.8	
3	"	1340	.408	41.3					54	5.4	
4	"	1409	.422	42.4					58	6.2	
5	"	1438	.433	42.4					59	6.5	
6	"	1508	.440	41.9					60	6.6	
7											
8											
9											
10											
EVAP.	10/11/65		STD								
BARR.	11/ 9/65		STD								
LAM.	11/10/65	1220	COPPER GRID - STD								

FIG. 17. GRADUAL RISE IN OUTPUT AFTER LAMINATION OF FRONTWALL MOLYBDENUM SUBSTRATE CELL WITH COPPER GRID HELD IN PRESSURE CONTACT.



TEST NO.	DATE	TIME	OCV	SCC	SERIES Ω	SHUNT Ω	SCC cm²	MAX. WATTS	% FILL	% EFF	REMARKS
1	9/13/65	1112									
2	"	1400									
3	9/14/65	0915									
4	9/15/65	1325								2.45	
5	9/16/65	1100								2.6	
6	9/20/65	1305								3.0	
7	9/24/65	0830								4.35	RELAMINATED 9/23/65
8	9/27/65	—								4.6	
9	10/8/65	1010								4.85	
10											
EVAP.	9/3/65	—	STD.								
BARR.	9/10/65	1330	STD.								
LAM.	9/13/65	1110	Cu GRID – CEMENTED WITH 3012 EPOXY								

FIG. 18. GRADUAL RISE IN OUTPUT OF FRONTWALL MOLYBDENUM SUBSTRATE CELL WITH EPOXY CEMENTED COPPER GRID (WALDMAN'S 3012 CONDUCTIVE EPOXY)

Figure 19 shows another "transient" effect occurring in the first few days of cell life. It is most noticeable for those cells with very high initial outputs. The current starts out, about 2 to 3 hours after lamination, at a very high level (25 mA/cm^2 is not uncommon), but the open circuit voltage is relatively low, 0.40 to 0.45 volts. The current drops steadily in the next few days to some lower level which it may hold indefinitely, while the voltage continues to rise. In some cases the voltage rises at about the same rate as the current drops so that the maximum power remains relatively unchanged. In other cases the current drops more rapidly and the maximum power may drop by 10 to 20% in the first week or so before leveling out. This is the more usual case for the 6, 7, and 8% cells that have been fabricated in recent months. In only one instance have we observed a cell that was greater than 7% efficient initially that has remained greater than 7% after 5 months of life. This was a plastic substrate cell. This was cell A535-1 which initially gave a peak output of 7.6% and which now, 165 days later, is giving 7.1%.

At first it was wondered whether this second type of transient behavior was also an instance of stress relaxation, or a case of continued diffusion of a particularly favorable impurity concentration gradient in the barrier region as advanced by Hill.[50] To check this point, different cells have been relaminated after they have undergone such an initial adjustment.

For example, cell D81G was 50 cm^2 area cell that was fabricated 8/30/65. It was 6.9% efficient 2-1/2 hours after lamination. It climbed to a maximum of 7.0% efficiency 2 hours later with an OCV of 0.485 volts, an SCC of 1.015 amperes and a fill factor of 72%. Thereafter the voltage held up at the 0.485 to 0.487 level while the current dropped steadily. This caused a steady drop in efficiency to 6.7% on 8/31, to 6.0% on 9/8, to 5.8% on 9/22, to 5.65% on 10/6 and to 5.5% on 11/10. At this time it was relaminated and it came back to 6.9% efficiency 2 hours after relamination with an OCV of 0.480 and an SCC of 1.030.

Thus, it does appear that this second type of transient behavior is also mechanical in nature and does not represent an intrinsic change in the barrier of the cell.

4. Cells with Epoxy Cemented Grids

The method of attaching the metal mesh grids to the barriers of cells by cementing with conductive epoxy adhesive was developed as a possible means of preventing the short circuits which occurred on many cells with pressure contact grids on extended thermal cycling test. When the difficulty with the loosening of the pressure contact grids came to light, it was expected that the epoxy cemented grids would be a solution to this problem also.

The first cemented copper grid cells were no more stable on shelf storage than the pressure contact gridded cells. It was found that the epoxy cement did not bond to the copper grids, and hence these cells in effect were also pressure contact gridded cells.

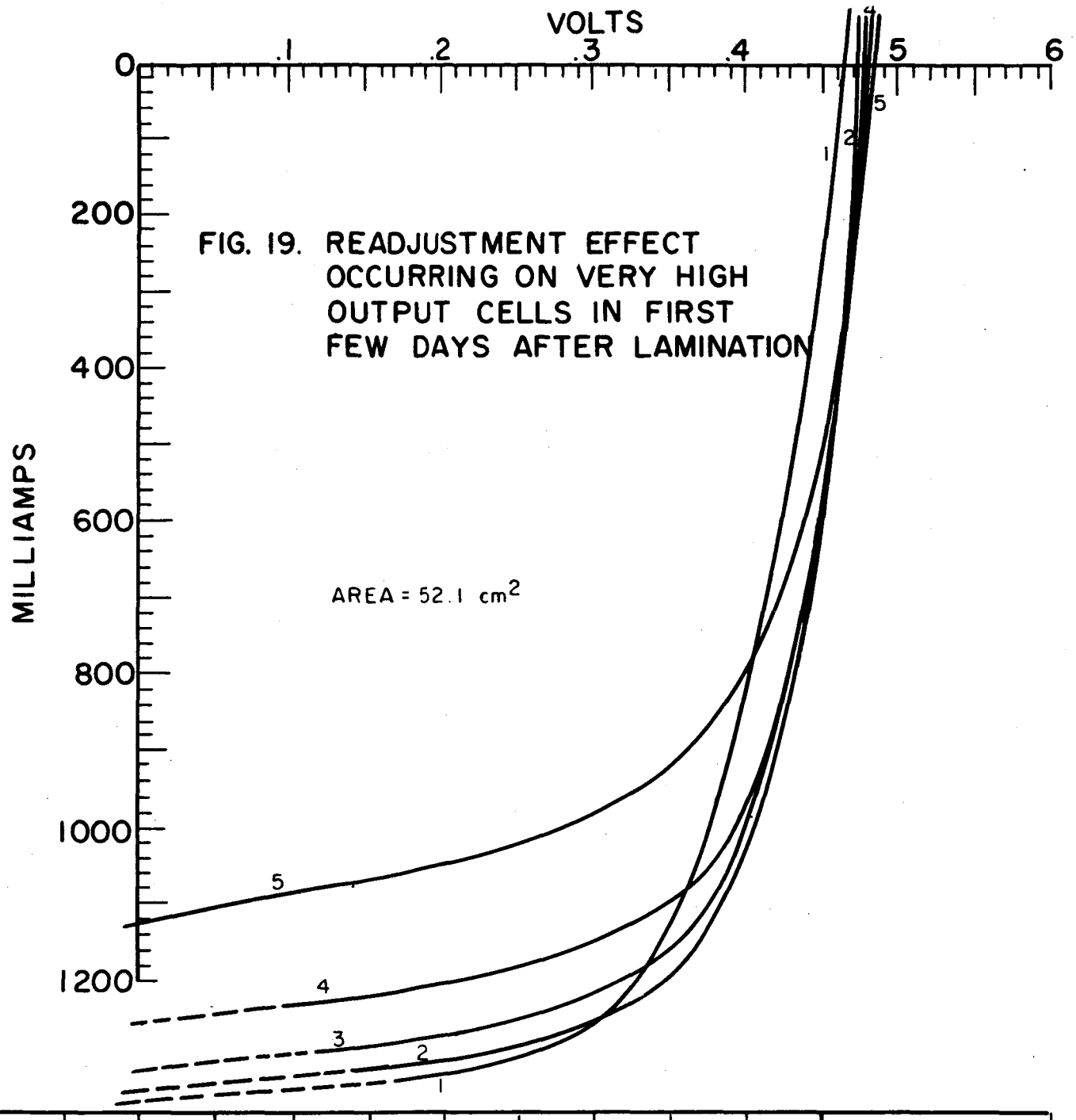


FIG. 19. READJUSTMENT EFFECT OCCURRING ON VERY HIGH OUTPUT CELLS IN FIRST FEW DAYS AFTER LAMINATION

TEST NO.	DATE	TIME	OCV	SCC	SERIES Ω	SHUNT Ω	SCC cm²	MAX. WATTS	% FILL	% EFF	REMARKS
1	8/31/65	1208	.462	1350			25.9	0.389	61	7.6	
2	"	1410	.471	1340			25.7	0.400	63	8.20	
3	"	1545	.477	1320			25 3	0.380	62	7.9	
4	9/1/65	0755	.480	1250			24.0	0.380	63	7.6	
5	9/8/65	1035	.483	1125			21.6	0 320	59	6.3	
6											
7											
8											
9											
10											
EVAP.	8/23/65	–	STD.								
BARR.	8/30/65	–	HI PRE-ETCH STD. BARRIER								
LAM.	8/31/65	10:05	STD.								

When the copper grids were silver plated, it was found that the epoxy cement did bond to them. There are only preliminary data available so far on the shelf stability of these epoxy cemented silver plated grids, but these cells also appear to be exhibiting a slow steady drop in output on shelf storage. The data are given in Table XII. There is an indication from more recent data, however, that the epoxy cement of these earlier cemented grid cells was not completely cured, and that this might have resulted in some relaxation of the grid contact.

b. Temperature Cycling

Solar cell panels on a space vehicle in orbit around the earth experience extremes of hot and cold temperature as the vehicle alternates between full sunlight and earth shadow. A 90 minute orbit represents about 5700 complete temperature cycles which may range from as low as -60 to -100°C and as high as +60 to +80°C, depending on the absorption-emission characteristics of the panel. Consequently, the ability of any new design solar cell or solar cell array to withstand prolonged temperature cycling is an important characteristic which must be assured before the new cell can be accepted for space application.

The Energy Conversion Laboratory at Lewis Research Center, NASA, has conducted thermal cycling tests of a number of different thin film CdS solar cell designs,[44] and a large number of tests of the front-wall molybdenum substrate cell with pressure contact grids of both the gold and copper variety. Early pressure contacted cells of 2 to 3% efficiency all failed within a few hundred cycles due to short circuits which developed between the grid and the cell. A few of the first Clevite 4 to 5% cells withstood nearly 3000 cycles on this test, but later cells of presumably the same design failed due to shorting in a few hundred to a thousand cycles.

On the other hand no cells with electroplated grids or epoxy cemented grids have failed due to short circuits, and a few plastic substrate cells have survived more than 10,000 cycles without shorting or degradation.[44] The electroplated grid cells have all been lower output cells, on the order of 2 to 3%. Only a few of the plastic substrate cells have been tested to date.

While the epoxy cemented grid cells did not develop shorts, they did degrade steadily to values of 1/4 to 1/2 of their initial output within a few hundred cycles.[51] Yet, when the cells were removed from the test chamber, they recovered soon afterwards to their original output levels. Another novel feature of the behavior of these cells was that it was only the voltage output that dropped. The current stayed up to nearly the full initial value.

At first it was thought that the drop in output of the epoxy cemented cells must be due to poor bonding of the epoxy cement to the copper grids. Then, when the same behavior was experienced on cells with silver plated copper grids, it was thought that insufficient cure of the epoxy might be the answer.

TABLE XII

SHELF STABILITY OF LARGE AREA FRONTWALL METAL SUBSTRATE CdS THIN FILM SOLAR CELLS WITH EPOXY CEMENTED GRIDS

Cell No.	Initial	1 Wk.	2 Wks.	1 Month	2 Months	3 Months
D41H	4.95%	4.6%	4.4%	4.4%	4.25%	3.95%
D58C	6.0	5.7	5.7	5.5	5.2	5.05
D60B	5.8	5.1	5.0	4.8	4.5	4.15
D85F	5.9	5.6	--	4.95	4.6	--

Notes:

Frontwall molybdenum substrate cells with silver plated copper grids attached using Waldman's No. 3021 conductive epoxy cement.

Epoxy cement cured during cell lamination -- cure may not have been complete.

From the markedly different behavior of the epoxy cemented grid cells on thermal cycling it is clear that a different type of degradation is being experienced. Initial indications point to stress induced defects resulting from the expansion or contraction of the adherent grid relative to the cell barrier over the wide temperature swings, but more detailed analysis and corroborating experiments are needed.

c. Moisture

The effect of moisutre on CdS barriers has been observed to be harmful by many investigators. The effect appears to be the same for single crystal cells and for polycrystalline film cells. Early studies indicated that moisture degraded CdS cells could be restored by simply driving off the moisture with heat.

Recently, it has been observed[52] that frontwall metal substrate film cells could not be restored if degraded beyond a certain point. This is contrary to earlier experience on backwall glass substrate thin film cells, and hence it was suspected that this might be another instance of the cell package failing.

This seemed likely in view of the observation that most of the CdS film cells with pressure contact grids had a large portion of the grid contact blocked by an intervening layer of Capran adhesive. A check of the manufacturer's literature on the Capran plastic revealed that this material is hygroscopic and will swell with moisture absorption. This readily explains the apparent irreversibility of the cells when a certain level of moisture degradation is exceeded.

To verify this hypothesis, several cells with grids attached by conductive epoxy cement were deliberately exposed to 80% humidity at 30°C for a week. These cells degraded to less than 2% output from initial levels between 5 and 6%. Some of the cells delaminated and the leads which had been held in pressure contact by the package came loose. Figure 20 shows the steady decrease in output that occurred for one of these cells. The others had a similar pattern of degradation. The cells were then removed from the test, dried, and relaminated. The outputs in all cases came back to about the same level as they were before the test.

An experiment was run to measure the degree of protection afforded the CdS film cell by various types and thicknesses of plastic encapsulation. One 3" x 3" cell was cut into quarters prior to lamination and then laminated with one portion in standard 2 mil Mylar, two in 14 mil Mylar and one in 10 mil Kel-F.

One 14 mil Mylar sample was kept in a desiccator as a control while the other three cells were kept in an 80% humidity chamber at 30°C. The cells were removed and measured after 1 week and after 2 weeks. The data are given in Table XIII. The output of the control sample actually increased from 5. 8% to 6. 2%. The cell in 10 mil Kel-F degraded from 6. 2% to 5. 3% to 4. 8%. The other cells degraded to less than 0. 5% within a week.

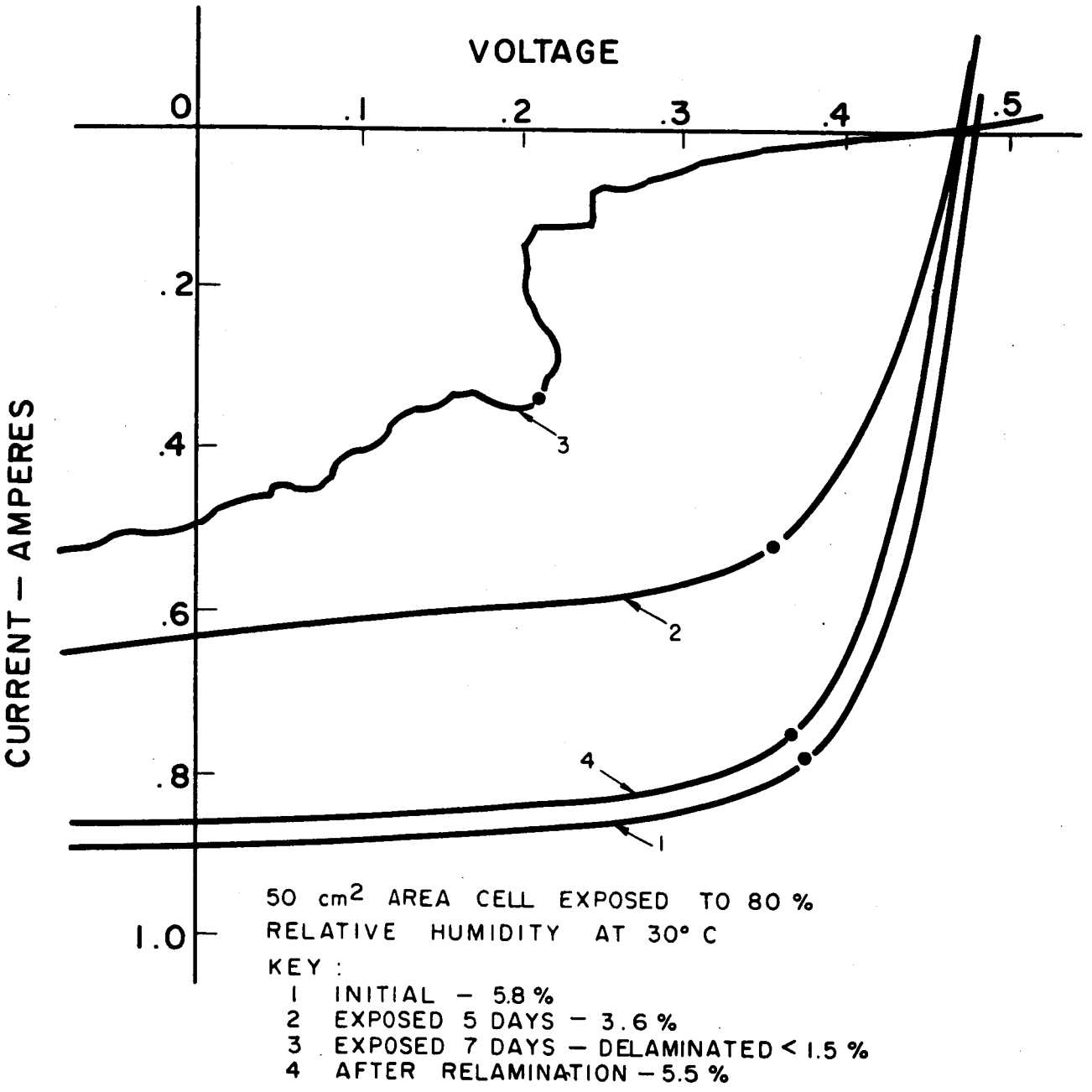


FIG. 20. MOISTURE DEGRADATION OF OUTPUT AND RECOVERY BY RELAMINATION OF CdS THIN FILM CELL WITH CEMENTED GRID

TABLE XIII

MOISTURE DEGRADATION TEST -- VARIOUS ENCAPSULANTS

Cell No.	Encapsulation	Storage	Efficiency at: Initial	1 Week	2 Weeks
B366A1	.014" Mylar	Desiccator - 25°C	5.8%	5.8%	6.2%
B366A2	.014" Mylar	80% R.H. - 30°C	5.5	<0.5	<0.5
B366A3	.002" Mylar	80% R.H. - 30°C	5.5	<0.5	<0.5
B366A4	.010" Kel-F	80% R.H. - 30°C	6.2	5.3	4.8

d. Impurity Contamination

The rinsing operation after barrier formation has been studied because it is at this point in the process that residual impurity contaminants can be controlled. Widely different experiences have been observed under various rinsing conditions and it was thought that the rinsing might under some conditions remove beneficial species necessary for cell stability, as well as harmful contaminants.

Therefore several newly dipped barriers were boiled for 10 minutes in ultra pure water and the water was analyzed to determine what elements were extracted. Aluminum, manganese, magnesium and copper were found in significant amounts from plastic substrate cells and these plus molybdenum and iron were found to be extracted from molybdenum substrate cells. Significant amounts were defined as those showing at least 3 times the quantity detected in a control sample of the same water in which the cells were not placed.

These samples of cells whose barriers had been extracted in this manner were dipped back into solutions containing 1000 times the concentration of each of the cations found to be extracted in significant amounts and the cells were dried, heat treated, laminated, and tested. Only the cells that had been dipped into solutions containing aluminum and copper were below average output. The effect was largely felt in the initial output rather than on the rate of cell degradation, though it is possible that differences in degradation because of these trace amounts of impurities could be masked by other larger effects such as grid contact loosening.

LABORATORY STANDARD PROCESS CELL FABRICATION

A small scale laboratory cell assembly line was set up and operated for the fabrication of large area (50 cm^2) metal substrate and plastic substrate cells. This line served a number of purposes. It provided a means of standardizing cell design and cell fabrication processes, demonstrating the continuing state-of-the-art, providing a basis of comparison for experimental design or process variations, and it served as a source of cells for demonstration and test purposes and for samples submitted to the contract monitor. The line was particularly effective in providing information as to whether a new lot of raw materials or a new item of tooling, or some other minor variation introduced into the process for economic or convenience reasons was satisfactory or not.

a. Molybdenum Substrate Cells

The frontwall metal substrate laboratory line was started in the seventh month of the contract when the additional funding was made available, and it started out with a slump in cell output. This slump, to about 2/3 of the previous level, was apparently caused by attempts to re-tool a number of fabrication processes for handling greater quantities of cells, and it took about a month before all the "bugs" were ironed out of the fabrication process and cell outputs were back to the previous 5% level.

Table XIV lists the initial cell outputs on a month-to-month basis of the standard process metal substrate cells. In the 9th and 10th months, nearly twice as many "standard" cells were processed, about 2 per day, because of extra help from temporary summer employees. The efficiency level increased in the 10th and 11th months to greater than 5%. This resulted from a lowering of cell lamination temperature. However, when it became apparent that these improved initial efficiencies were at the expense of cell stability, the lamination temperature was increased during the last month, and hence the average efficiency dropped.

For the 5 month period 131 "standard" construction cells were made and these averaged 5.6% in efficiency with only 4 cells being less than 4%. A total of 64 of these cells were furnished to the Contract Monitor.

In addition, there were a total of 64 standard large area frontwall molybdenum substrate cells encapsulated in Kapton (H-Film) plastic in this period. These averaged 3.9% with a minimum of 1.5% and a maximum of 5.7%. Of these 28 were delivered to the Contract Monitor. The output on these cells is less because approximately 20% of the photoeffective wavelength light is absorbed by the covering plastic layer. Also the Kapton plastic appears to be more difficult to laminate than Mylar.

b. Plastic Substrate Cells

The improved frontwall plastic substrate cell was developed late in the sixth month of the contract and the process was standardized accordingly and the laboratory line operated on this basis for the last 6 months. The data on this line are listed in Table XV. There was a reasonably steady improvement in reproducibility and average performance over the period. A total of 114 cells were fabricated with an overall average efficiency of 5.4%. There were 7 cells of less than 4% efficiency. Of these cells 42 were furnished to the Contract Monitor.

TABLE XIV

OUTPUT OF STANDARD PROCESS LINE - MOLYBDENUM SUBSTRATE CELLS
(50 cm^2 Cells, Mylar Encapsulated, 60 lpi Copper Grids)

Cell Efficiency	Month 8	Month 9	Month 10	Month 11	Month 12	Total
< 4.0%		4				4
4.0		1				1
4.1						
4.2						
4.3	2	2				4
4.4		2				2
4.5		2				2
4.6		3				3
4.7	3	1				4
4.8	3	3	1		1	8
4.9		3		1		4
5.0	2	2				4
5.1	2	2			1	5
5.2	2	1	1			4
5.3	5			2	1	8
5.4	2	2	3	2	1	10
5.5	1		2	2		5
5.6	1	1	2		1	5
5.7		2	1	1		4
5.8	2	2	2	2		8
5.9			3	1	1	5
6.0		3		1	1	5
6.1		1	3	3		7
6.2			2			2
6.3		1		2		3
6.4		2	4	1		7
6.5		1	3	1		5
6.6			2	2		4
6.7			2			2
6.8		1				1
6.9				1		1
7.0			2	1		3
7.1						
7.2			2			2
7.3						
7.4			1	1		2
7.5						
7.6						
7.7						
7.8			1			1
No. of cells	25	38	37	24	7	131
Avg.	5.1	5.2	6.2	6.0	5.4	5.6

TABLE XV

OUTPUT OF STANDARD PROCESS LINE PLASTIC SUBSTRATE CELLS
(50 cm^2 Cells, Mylar Encapsulated, 60 lpi Copper Grids)

Cell Efficiency	Month 7	Month 8	Month 9	Month 10	Month 11	Month 12	Total
< 4.0%			4	1	1	1	7
4.0	1					1	2
4.1					1		1
4.2			2				2
4.3							
4.4			1				1
4.5			2	1	1		4
4.6	1		3		1	1	6
4.7		1	2				3
4.8			2	1			3
4.9		1	3	1		1	6
5.0	1	3	2	2		2	10
5.1	2			2		1	5
5.2		2	1		1		4
5.3	1		2	3	1		7
5.4		3	1	1	3	2	10
5.5							
5.6				1	1	4	6
5.7	1	2			3	1	7
5.8		1	1	1		3	6
5.9		1	3		1	2	7
6.0			1				1
6.1						1	1
6.2			2	1	1	2	6
6.3							
6.4							
6.5						1	1
6.6							
6.7				2		1	3
6.8							
6.9						1	1
7.0						1	1
7.1		1				1	2
7.2							
7.3							
7.4							
7.5							
7.6					1		1
No. of cells	7	15	32	17	16	27	114
Avg.	5.0	5.4	4.9	5.5	5.5	5.7	5.4

REFERENCES

1. Contract NAS 3-2795. Final Report: W. J. Deshotels and F. Augustine, "Study of Thin Film Large Area Photovoltaic Solar Energy Converter," NASA CR 54343, October 30, 1964.

2. A. Carlson, "Research on Semiconductor Films," WADC Technical Report 56-52, January, 1956.

3. H. I. Moss, "A Broad Area CdS Photovoltaic Cell," Proceeding of the National Airborne Electronics Conf. (NAECON), May, 1960.

4. A. E. Middleton, et al., "Evaporated CdS Film Photovoltaic Cells for Solar Energy Conversion," Amer. Rocket Soc. Conf. Paper 1291-60, Santa Monica, California, September, 1960, Published in "Energy Conversion for Space Power" edited by N. W. Snyder, Academic Press 1961.

5. "Solar Cell Array Optimization," ASD Technical Documentary Report ASD-TR-61-11, Vol. III, December, 1962.

6. F. A. Shirland, et al., "Research on Solar Energy Conversion Employing Cadmium Sulfide," ASD Technical Documentary Report ASD-TR-62-69 Vol. I, January, 1962, pp. 18-20.

7. "Kapton" plastic obtainable from E. I. DuPont, Wilmington, Delaware.

8. ref. 6, pp. 20-26.

9. F. A. Shirland, et al., "Research on Solar Energy Conversion Employing Cadmium Sulfide," ASD-TR-62-69, Vol. II, December, 1962, pp. 24-5.

10. Electroformed Metal Mesh obtainable from Buckbee Mears Co., St. Paul, Minnesota.

11. ref. 6, pg. 6.

12. T. A. Griffin, et al., "Research and Development in CdS Photovoltaic Film Cells," NASA CR-54481, August, 1965, pp. 23-4.

13. F. A. Shirland and J. R. Hietanen, "Improved CdS Thin Film Solar Cells," Proc. 19th Annual Power Sources Conf., May, 1965.

14. ref. 6, pg. 23.

15. F. A. Shirland and J. C. Schaefer, "Cadmium Sulfide Film Photovoltaic Cell Assemblies," Contract No. NAS 3-1850, February, 1962, pp. 10-11.

16. T. A. Griffin, et al., "Research and Development in CdS Photovoltaic Film Cells," NASA CR-54108, June, 1964, pg. 19.

17. Grade MD 750 Silver Flake obtainable from Metals Disintegrating Co., Elizabeth, New Jersey.

18. Pyre M. L. Varnish obtainable from E. I. DuPont Co., Wilmington, Delaware.

19. J. S. Skarman, et al., "Investigation of Chemically Sprayed Thin Film Photovoltaic Cells," Technical Report AFAPL-TR-65-64, June, 1965, pp. 49-52.

20. M. G. Miksic, et al., "Behavior of CdS Thin Film Transistors," Solid State Electronics, Vol. 7, 1964, pp. 39-48.

21. R. S. Muller and R. Zuleeg, "Vapor Deposited Thin Film Heterojunction Diodes," J. Appl. Phys. Vol. 35, 1964, pp. 1550-56.

22. R. Belt, et al., "Investigation of CdS Thin Film Solar Cells," Technical Report AFAPL-TR-65-1, February, 1965, pp. 85-6.

23. D. C. Reynolds, "The Photovoltaic Effect in Cadmium Sulfide," Phys. Rev. 96, October, 1954, pp. 533-4.

24. D. C. Reynolds, "Cadmium Sulfide Barrier Layer Cell," U. S. Patent 2, 844, 640, July 22, 1958 and U. S. Patent 2, 981, 777, April 25, 1961.

25. D. A. Hammond, et al., "A Cadmium Sulfide Solar Generator," Technical Report WADC TR 57-770, pp. 58-63, December, 1957 (AD-151036).

26. F. A. Shirland and Arnold R. Rom, French Patent 1, 336, 191, February 11, 1964.

27. ref. 25, pp. 65-67.

28. F. A. Shirland, "Vacuum Evaporated Barrier for a CdS Crystal," U. S. Patent 3, 146, 138, August 25, 1964.

29. ref. 25, pp. 63-65.

30. R. R. Chamberlin, et al., "Feasibility Investigation of Chemically Sprayed Thin Film Photovoltaic Converters," Technical Documentary Report ASD-TDR-63-222, Part I, pg. 78, March, 1963.

31. J. E. Hill, et al., "Process for Making Conductive Film," U. S. Patent 3, 148, 084, September 8, 1964.

32. ref. 9, pg. 8.

33. D. A. Cusano, "CdTe Solar Cells and Photovoltaic Heterojunctions in II-VI Compounds," Solid State Elect. 6, pp. 228-9, 1963.

34. W. J. Deshotels and F. Augustine, "Study of Thin Film Large Area Photovoltaic Solar Energy Converter," NASA CR-54343, pg. 20, October, 1964.

35. ref. 13.

36. ref. 9, pp. 24-5.

37. ref. 10.

38. ref. 6, pp. 28-32.

39. S-122 Fluorocarbon Release Agent Dry Lubricant obtainable from Miller-Stephenson Chem. Co., Chicago, Illinois.

40. R. W. Aldrich and D. A. Cusano, "Research on Thin Film Polycrystalline Solar Cells," Technical Report AFAPL-TR-65-8, pp. 133-41, February, 1965.

41. L. D. Massie, "Review of Progress on the CdTe Thin Film Solar Cells," paper presented at 5th Photovoltaic Specialists Conf., Goddard Space Flight Center, NASA, October, 1965. Proceedings to be printed by PIC.

42. M. Wolf and H. Rauschenbach, "Series Resistance Effects on Solar Cell Measurements," Advanced Energy Conversion 3, 455-79, 1963.

43. ref. 12, pp. 18-23.

44. A. E. Spakowski, et al., "Some Problems of the CdS Solar Cell," paper presented at 5th Photovoltaic Specialists Conf., Goddard Space Flight Center, NASA, October, 1965, NASA TMX-52144.

45. E.-Solder 3021 Silver Epoxy obtainable from Epoxy Products Inc., Irvington, New Jersey.

46. Hamilton Watch Co., Lancaster, Pennsylvania.

47. 500 watt Photoflood, G. E. Co., Type FBJ.

48. F. A. Shirland, et al., "Thin Film CdS Frontwall Solar Cells," American Rocket Soc. Conf. Paper 2566-62, Santa Monica, California, September, 1962, Published in "Power Systems for Space Flight" edited by M. A. Zipkin and R. N. Edwards, Academic Press, 1963.

49. E-Solder 3012 Silver Conductive Epoxy obtained from Epoxy Products Inc., Irvington, New Jersey.

50. E. Hill and B. Keramidas, "A Model for the CdS Solar Cell," Paper presented at 5th Photovoltaic Specialists Conf., Goddard Space Flight Center, NASA, October, 1965, Proc. to be printed by PIC.

51. Verbal Communication, A. E. Potter, Jr., Lewis Research Center, NASA.

52. A. E. Potter, Jr., Panel Discussion "Problems and Future Possibilities of Thin Film Solar Cells," 4th Photovoltaic Specialists Conf., Lewis Research Center, NASA, June, 1964. Proceedings printed by PIC, pg. B-5.

ABSTRACT

The frontwall plastic substrate CdS thin film solar cell has been developed to the point where 50 cm^2 area cells can be fabricated in the laboratory with initial conversion efficiencies of 4 to 6%. A few cells have been made with outputs up to 8%. The thickness and weight of the cells have been reduced and a maximum power to weight ratio of 106 watts per pound has been achieved for a 50 cm^2 area cell.

Studies indicate that the frontwall metal and plastic substrate cells are essentially equivalent. Some of the cells have been stable at the 4 to 5% level for periods of a year, but others have not. Some cells have been stable on prolonged temperature cycling test, but others have not. Indications are that the present Clevite process yields cells whose barriers are intrinsically capable of converting 6 to 8% of the solar energy incident on them, and that these barriers are inherently stable. The limitations of the present cell package are believed to be preventing the reproducible attainment of 6 to 8% efficiencies on a stable basis.